



The deactivation of Cu–Co alloy nanoparticles supported on ZrO₂ for higher alcohols synthesis from syngas



Gui-Long Liu^{a,b}, Ting Niu^{a,b}, Ang Cao^{a,b}, Yu-Xia Geng^c, Yuan Zhang^c, Yuan Liu^{a,b,*}

^aTianjin Key Laboratory of Applied Catalysis Science and Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

^bCollaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China

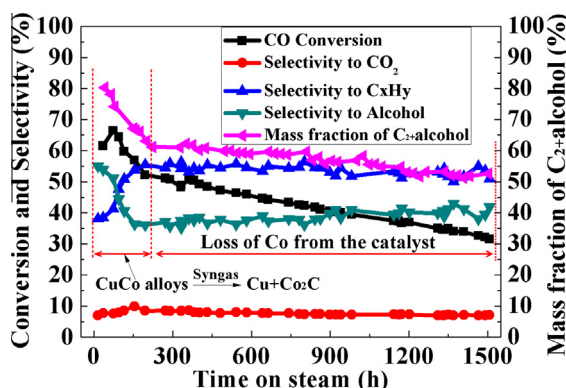
^cChina Tianchen Engineering Corporation, Research and Development Center, 1# Jingjin Road, Beichen District, Tianjin 300400, China

HIGHLIGHTS

- The deactivations of Cu–Co/ZrO₂ for higher alcohols synthesis were investigated.
- Phase separation and volatilization of cobalt are the major causes for the catalyst deactivation.
- Sintering and coke deposition are not responsible for the deactivation.
- CO₂C might suppress the decomposition of Cu–Co alloy and volatilization of cobalt.

GRAPHICAL ABSTRACT

Deactivation of the Cu–Co/ZrO₂ catalyst was mainly attributed to volatilization of cobalt species. CO₂C might play a protective role for the decomposition of Cu–Co alloy and volatilization of cobalt species.



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ABSTRACT

The deactivations of Cu–Co alloy nanoparticles supported on ZrO₂ for higher alcohols synthesis from syngas were investigated. The catalysts after reaction for 200 and 1500 h were compared and characterized by using N₂ adsorption and desorption, X-ray diffraction, transmission electron microscopy, energy dispersive spectrometer, inductively coupled plasma mass spectrometry and thermo gravimetric analysis techniques. The characterization results showed that the deactivation of the Cu–Co/ZrO₂ catalyst in the reaction period of 200–1500 h was mainly attributed to cobalt volatilization in the form of its carbonyl at the reaction temperature. Sintering of the Cu–Co alloy and coke deposited on the catalyst surface could hardly be observed, meaning that sintering and coke deposition are not responsible for the deactivation of the catalyst. At the same time, the formation of CO₂C on the surface of Cu–Co alloy might play a protective role for the decomposition of Cu–Co alloy and the volatilization of carbonyl cobalt. According to the results, some possible recommendations were proposed for the design of Cu–Co-based catalysts.

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* Corresponding author at: Tianjin Key Laboratory of Applied Catalysis Science and Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China. Tel.: +86 022 87401675.

E-mail address: yuanliu@tju.edu.cn (Y. Liu).

1. Introduction

Higher alcohols, which refer to alcohols other than methanol, can be used as fuels, fuel additives, chemicals and chemical raw materials [1–3]. Higher alcohols synthesis (HAS) from syngas has been the focus of attention in a few decades, while the commercialization of this process is still difficult because of the low selectivity to higher alcohols and/or poor stability of the catalysts [4,5].

The catalysts reported for HAS include mainly four types, the modified methanol catalysts, the modified Fischer–Tropsch synthesis catalysts, the Mo-based catalysts and the Rh-based catalysts. Supported Rh catalysts show relatively high selectivity to ethanol; however the high price and the limited availability of Rh restrict their industrial applications [6,7]. As for the modified methanol catalysts, methanol is the major product [8,9].

Owing to the excellent resistance to sulfur poisoning [10–12], Mo-based catalysts have attracted much attention and the deactivation of the catalysts were studied in a few reports. Surisetty et al. [13] reported that the alkali-promoted Co–Rh–Mo/carbon nanotubes (CNTs) catalyst showed two different deactivation steps during 720 h of continuous reaction: the loss of sulfur from MoS₂ on the surface of the catalyst and sintering of metal sulfides located on the outer surfaces of the CNTs. Hensley et al. [14] found that the deactivation of the Mo-based catalysts are ascribed to oxidization and carburization of molybdenum resulted from sulfur deprivation, coking of the catalyst surface and the segregation of cobalt into crystalline Co₉S₈. They also pointed out that only when the catalyst was continuously vulcanizing, selectivity to alcohols could be maintained for thousands of hours. Even though the Mo-based catalysts can be stabilized by continuously vulcanizing, sulfur species would be brought into the alcohols as a contaminant, which is a critical drawback for Mo-based catalysts.

Among the four types of catalysts, modified Fischer–Tropsch catalysts are most attractive, owing to their high activity and comparatively high selectivity to higher alcohols at mild reaction conditions [15–17]. Modified Fischer–Tropsch catalysts include Cu–Fe and Cu–Co based catalysts. In the early years, studies were concentrated on the reaction mechanism and the relation of the catalyst structure with the catalytic performance. Although the details of the mechanism are still under disputation, the following viewpoints have been accepted commonly. For Cu–Co and Cu–Fe based catalysts, metal copper can activate CO non-dissociatively and favors the formation of alcohols, while metal cobalt/iron enables the dissociative adsorption of CO and C–C chain growth [1,18–20]. Higher alcohols generated under the synergistic catalyzing by Cu and Co/Fe, and the interaction between Cu and Co/Fe is critical on the catalytic performance for the synthesis of higher alcohols, especially for the selectivity to higher alcohols [16,18,21,22]. After several decades of researches, some catalysts with good activity and excellent selectivity have been reported, unfortunately, the reported catalysts are not stable enough for practical application.

To investigate the deactivation of Cu–Fe catalysts, Xiao et al. [16] prepared a model catalyst of CuFe bimetallic nanoparticles, in which Cu and Fe were homogeneous dispersed; while in the reaction process, the copper–iron bimetallic nanoparticles were separated into monometallic Cu nanoparticles, Fe₃O₄ nano rods and χ -Fe₅C₂ under syngas; the phase separation of Cu–Fe nanoparticles weakened the synergy between Cu and Fe and resulted in a decreased selectivity to higher alcohols with time on steam. Sun et al. [15,23] reported a Zn-promoted CuFeMnZrO₂ catalyst, over which, the selectivity to total alcohols was 55%, the mass fraction of higher alcohols in the total alcohols was 45% (the other 55% is methanol) and the catalyst showed excellent stability during the running of 2400 h; they attributed the good stability to the homo-

geneous distribution of the active sites and atomic distances between these sites. This is a much promising catalyst, it would be better if the activity (CO conversion was about 25% over the Zn promoted catalyst) and the selectivity to higher alcohols can be elevated.

For Cu–Co based catalysts, it is recognized that the formation of Cu–Co alloy is much important for the selectivity to higher alcohols, as stated above and details can be seen from literatures [1,19,24–26]. Thus, in recent years, designing and preparing bimetallic nano Cu–Co alloy catalysts have been the focus for Cu–Co based catalysts. To facilitate the formation of Cu–Co alloy, CuCoO₂ [24], CuCo₂O₄ [22,27,28], LaCo_{1-x}Cu_xO₃ [29,30] and CuCoAl–LDH (stands for layered double hydroxide contains copper, cobalt and aluminum ions) [31] were used as the catalyst precursors, because in which Cu and Co can be uniformly distributed at the atomic level and resultantly the formation of Cu–Co alloy is favored under reduction. For example, Gao et al. [31] demonstrated a preparation of core–shell Cu@(CuCo–alloy) nanoparticles via the reduction of CuCoAl–LDH nanoplatelets, over the catalyst with a ratio of Cu/Co = 1:2, the selectivities to alcohols in the carbon containing products and higher alcohols in the total alcohols were 50.6% and 80.8 wt.%, respectively, which are very high. Similarly, the Cu–Co alloy derived from LaCo_{0.7}Cu_{0.3}O₃ supported on ZrO₂ showed high activity with CO conversion of 35.3%, very high selectivities to alcohols of 43.4% and the mass fraction of higher alcohols was 82.3 wt.% in the total alcohols [30]. The studies indicate that the Cu–Co alloy based catalysts possess high selectivity to higher alcohols and high activity. If this kind of catalysts have qualified stability, commercialization of HAS would be promising in the near future.

Although numerous studies have been devoted to the investigation of Cu–Co catalysts, investigations on the deactivation of Cu–Co catalysts are comparatively rare and the deactivations of the Cu–Co catalysts are still not thoroughly investigated. Yang et al. [32] prepared a CuCo/TiO₂ catalyst using the deposition–precipitation method; after reaction for 144 h, severe sintering occurred and Co_xC formed on the catalyst surface, they pointed out that both of which reduced the number of surface Co atoms and led to the catalytic deactivation. Courty et al. [5,33] reported a catalyst of Cu–Co/Zn/Al₂O₃ with a LDH structure prepared by co-precipitation method, and found the catalytic performance of the catalyst for HAS decreased with time on steam; they speculated that the deactivation of the catalyst was caused by the coke deposition, separation of Co from originally homogeneously distributed Cu–Co phase, and the loss of Co caused by the formation of volatile cobalt carbonyl. Xu et al. [34,35] prepared a K-doped Cu–Co/ZnO/Al₂O₃ catalyst using a co-precipitation method; after reaction for 4000 h, coke deposition on the surface of the catalyst, decrease of the surface area, separation of Cu and Co active sites, and separation of ZnO from the Zn-rich Zn–Al support were observed; they concluded that all the above causes might contribute to the deactivation of the catalyst.

In summary for the deactivation of Cu–Co based catalysts, sintering, coke deposition, phase separation of Cu–Co alloy and loss of Co are the main causes. While, among the four deactivation causes, which is the key cause has never been specified, and the specific deactivation reasons are dependent on the preparation method and composition of the catalyst.

In our previous work, ZrO₂ supported LaCo_{1-x}Cu_xO₃ were prepared and used as the catalysts for higher alcohols synthesis. After reduction, nanoparticles of Cu–Co alloy were highly dispersed on La₂O₃-doped ZrO₂, and the catalyst showed very good activity and much high selectivity to higher alcohols [30].

In this work, deactivation of the Cu–Co/ZrO₂ was studied and some possible recommendations were proposed for the design of Cu–Co based catalysts.

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