



## Effect of $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_5$ on the performance of Ru–Zn catalyst for benzene selective hydrogenation to cyclohexene

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### ABSTRACT

A series of Ru–Zn catalysts with different Zn contents were prepared by co-precipitation. The catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) – Ar<sup>+</sup> sputter, transmission electron micrographs (TEM)–energy dispersion scanning (EDS) and temperature-programmed reduction (TPR). The performances of the catalysts for benzene selective hydrogenation to cyclohexene were investigated in the presence of 0.6 mol/L of ZnSO<sub>4</sub>. The results showed that the Ru and Zn in Ru–Zn catalyst were in metallic Ru and ZnO respectively and the ZnO was rich on the surface. The ZnO alone could not improve the selectivity to cyclohexene of Ru–Zn catalyst. However, the ZnO on the surface could react with ZnSO<sub>4</sub> to form a  $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_5$  salt. The  $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_5$  salt chemisorbed played a key role in improving the selectivity to cyclohexene of Ru–Zn catalysts. After Ru–Zn(8.6%) catalyst was pretreated 22 h in ZnSO<sub>4</sub> solution at 140 °C and 5 MPa H<sub>2</sub>, a cyclohexene selectivity of 81.4% at a benzene conversion of 54.0% was achieved at 10 min and a maximum cyclohexene yield of 58.9% was reached. Moreover, the activity was stable above 50% and the cyclohexene selectivity and yield were steadily above 76% and 40% on this catalyst in the first six recycles, respectively.

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### 1. Introduction

There has been a growing interest in using heterogeneous catalysts for the selective hydrogenation of benzene to cyclohexene, a greener intermediate feedstock than cyclohexane for producing nylons and fine chemicals [1–6]. However, it is thermodynamically difficult to obtain cyclohexene in high selectivity. Therefore, it has been long time that only cyclohexane was obtained during the hydrogenation of benzene [7]. In 1989, the Asahi Chemical Industry Co. industrialized the process for producing cyclohexene from the partial hydrogenation of benzene employing an unsupported Ru–Zn catalyst, and a cyclohexene yield of 32% at a benzene conversion of 40% was obtained [8,9]. However, the yield of cyclohexene is still relatively low. Therefore, it is necessary to study catalyst preparation and modification in order to increase the yield of cyclohexene.

Some additives, which are directly put into the reaction system together with the catalyst and sometimes are called co-catalyst [8] and reaction modifier [10], can greatly improve the selectivity to cyclohexene. Generally, there are two kinds of additives:

organic [4,11–13] and inorganic [8,14,15]. Effective organic additives should contain a polar group such as hydroxyl or amine group. However when using these organic additives the selectivity to cyclohexene never exceeded 40%. Inorganic additives such as Zn, Fe, Co, Ni, Cd, Ga, and In salts are more effective than organic additives [14]. Among them, ZnSO<sub>4</sub> has been regarded as the best additives. Struijk et al. [14] used XPS to characterize Ru catalyst after hydrogenation in the presence of ZnSO<sub>4</sub> under the reaction conditions of 423 K and 5.0 MPa of H<sub>2</sub>, and found the majority of chemisorbed Zn is present as Zn<sup>2+</sup>. They suggested that the chemisorbed Zn<sup>2+</sup> could enhance the hydrophilicity of Ru catalyst and selectively cover the most reactive sites, which improved selectivity to cyclohexene of Ru catalyst. Based on these, they specially pointed out the salts as effective additives should have a high absorbability on ruthenium surface and a difficult reduction ability under the reaction conditions.

The promoters also have great impacts on the yield of cyclohexene. It was reported that K [16], Fe [17–19], Co [13,20], Ce [21], Ba [22], La [15,23,24] and Zn [4,8,25–29] as a promoter or co-promoters to modify the ruthenium by co-precipitation or co-impregnation or other methods were beneficial for the increase of the selectivity to cyclohexene. Among them, Zn has been considered to be the best promoter [4,8]. Wang et al. [26] and He et al. [28] prepared Ru–Zn/ZrO<sub>2</sub> catalysts using hydrogen reduction of

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