

Novel high efficiency steam reforming of acetic acid for hydrogen production by Cu–Zn–Co catalyst

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Introduction

Hydrogen is an important fuel that can be used in internal combustion engines or as the raw material for future economy [1]. Now most hydrogen is produced from fossil fuels such as natural gas, naphtha, and coal[2]. The world-wide interest in energy area now is strongly focused on the production of hydrogen from alternative fuels. Some methods of producing hydrogen from biomass have been investigated: for example, gasification [3] or flash pyrolysis of biomass to bio-oil and its steam reforming [4]. However, bio-oil was a complex mixture of oxygenate compounds, and design of an effective catalyst requires the use of model oxygenate components to establish structure activity correlations. Acetic acid was one of the major components in bio-oil [5,6]. In addition, acetic acid itself is renewable and can be easily obtained from biomass by fermentation, and acetic acid, unlike methanol and ethanol, is nonflammable, hence, it is a safe hydrogen carrier. Up to now, there are very limited works focused on producing hydrogen from acetic acid steam reforming, for example, ICI 46-1, UC G-90C, Ni–Al, Pt/ZrO₂, Pt, Rh and Pd based catalysts[5-8]. Usually, the temperature conducted in the reforming reactions over these catalysts was higher than 873 K, and there were always appreciable amounts organic compounds generation during the reactions, which resulted in the low selectivity to hydrogen. In this work, we reported a novel catalyst for steam reforming of acetic acid, Cu–Zn–Co catalyst, which was more active, selective and also very stable. In the temperature range of 573–673 K, acetic acid could be converted completely and selectivity to hydrogen exceeded 90%, to our knowledge, such results have not been reported at such low reaction temperature.

Materials and Methods

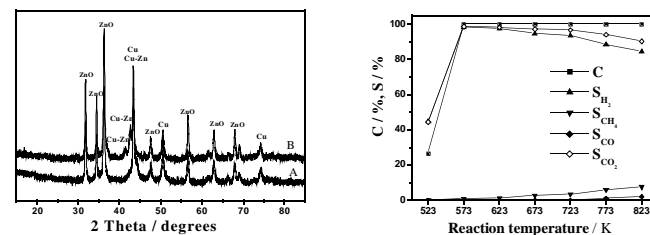
Catalysts were prepared by co-precipitation method. Catalytic performances tests were carried out in a fixed bed continuous flow quartz reactor at normal pressure. The gas phase effluents were analyzed on on-line chromatographs equipped with TCD detectors. Liquid products were separated and analyzed by means of a flame ionization detector (FID). The XRD measurements were performed on a Philips X pert MPD instrument using Cu K α radiation. The TPR experiments were carried out in a conventional flow system built in our laboratory. The XPS measurements were carried out at a room temperature on a VG ESCALAB 210 spectrometer, calibrated by the C1s binding energy of 285.0 eV. The BET area was measured by method on a Micromeritics ASAP-2010 at 77K with N₂ as the absorbent.

Results and Discussion

For the fresh catalysts, diffraction peaks attributed to Cu and ZnO phase were observed. While for the used catalyst, some new diffractions peaks were observed, centred at $2\theta = 41.4, 42.7$ and, 43.4° , were the characteristics of Cu–Zn alloy phase. It could be found that Cu–Zn sample showed two H₂-TPR consumption peaks at 579 and 1002 K. For Cu–Zn–Co catalyst, the reduction profile showed a shoulder at 553 K, a principal peak at 643 K and a long tail peak at 1023 K, which were corresponding to the reduction Cu, Co and Zn species,

respectively. XPS spectra indicated that Cu species existed as metal state whether in the fresh or used catalysts. The binding energy Co 2P_{3/2} indicated that Co species existed as the same state of CoO before and after the steam reforming reactions. The BET measurements indicated that the specific area of the Cu–Zn–Co catalyst was relatively little, 18.37 m² g⁻¹, and the total volume of pores and average pore diameter were 0.18 cm³ g⁻¹ and 33.33 nm, respectively.

Over Cu–Zn–Co catalyst, conversion of acetic acid increased rapidly with increasing temperature and reached 100% at 573 K, besides, selectivities to H₂ and CO₂ also increased sharply and reached the maximum values of 98.2 and 98.6%, respectively. Along with the temperature continuously increasing to higher ranges, the selectivities to CH₄ and CO reached a remarkable level, such as at 823 K, the selectivities to CH₄ and CO were 7.6 and 2.1%. The effects of LHSV on the catalytic performances of Cu–Zn–Co catalyst at 623 K showed that the catalyst exhibited good performance under the whole LHSV investigated. The conversions of acetic acid exceeded 90% and the selectivities to H₂ and CO₂ kept more than 94% even under the higher LHSV of 15.6 h⁻¹. With S/C decreasing, acetic acid conversions dropped substantially, which was accompanied by a pronounced amount of CO generation, especially at lower S/C of 2.5:1. As a result, the selectivity to H₂ decreased dramatically from 98.2 to 87.3%. Cu–Zn–Co catalyst maintained its activity and selectivities without any noticeable deactivation for all the time-on-stream under the reaction conditions over for 100 h. The conversions of acetic acid fluctuated but still kept about 100%.



Significance

We acknowledge the financial support of the 973 Project of China (G2003CB214503).

Figure 1 XRD patterns for the fresh and used Cu–Zn–Co catalysts (1:1:1). A: the fresh catalyst; B: the used catalyst. **Figure 2.** Effects of reaction temperature on the conversions of acetic acid and selectivities to the products. Experimental conditions: catalyst: Cu–Zn–Co (1:1:1); S/C mol ratio 7.5:1; LHSV = 5.1 h⁻¹; P = 1 atm.

References

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