

# Effect of preparation method of $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ on the catalytic performance in the oxidative dehydrogenation of n-butene

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## Introduction

Multicomponent bismuth molybdates have been widely investigated as efficient catalysts for the oxidative dehydrogenation of n-butene to 1,3-butadiene, and co-precipitation method has been generally employed for the preparation of multicomponent bismuth molybdate catalysts [1]. One of the major problems of co-precipitation method, however, is that all metallic cations are not precipitated at the same pH and temperature [2], implying that multicomponent bismuth molybdate catalysts prepared by a co-precipitation method are not molecularly homogeneous. This leads to low efficiency of metal components in the catalyst and lessens reproducibility of catalyst preparation. Single-step citric acid-derived sol-gel method has attracted much attention as a promising method for preparing fine metal oxide catalysts with high purity, high homogeneity, and high surface area [3]. Therefore, it is expected that a multicomponent bismuth molybdate catalyst prepared by a citric acid-derived sol-gel method would show an excellent catalytic performance in the oxidative dehydrogenation of n-butene. In this work,  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$  catalysts were prepared by a co-precipitation method and by a citric acid-derived sol-gel method for use in the oxidative dehydrogenation of n-butene. The effect of preparation method on the catalytic property and catalytic activity of  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$  catalysts was investigated.

## Materials and Methods

$\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -CP and  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -SG catalysts were prepared by a co-precipitation method and by a citric acid-derived sol-gel method, respectively. The prepared catalysts were characterized by XRD, ICP-AES, BET, and FE-SEM measurements. The oxidative dehydrogenation of n-butene to 1,3-butadiene was carried out in a continuous flow fixed-bed reactor in the presence of air and steam. Each catalyst was charged into a tubular quartz reactor and pretreated at 470 °C for 1 h with an air stream. The feed composition was fixed at n-butene: $\text{O}_2$ :steam=1:0.75:15.  $\text{C}_4$  raffinate-3 containing 57.9 wt% n-butene (1-butene (7.5 wt%) + trans-2-butene (33.9 wt%) + cis-2-butene (16.5 wt%)) was used as a n-butene source, and air was used as an oxygen source. The catalytic reaction was carried out at 420 °C. The contact time was maintained at 14.1 g-catalyst-h/n-butene-mole.

## Results and Discussion

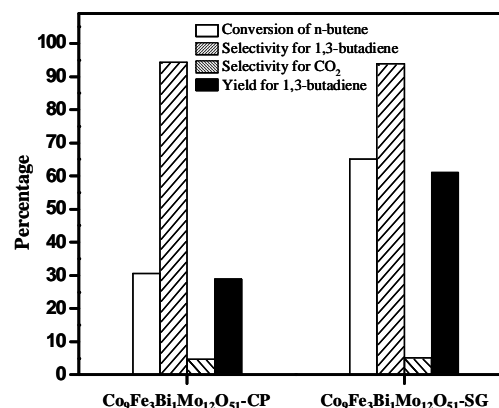
Figure 1 shows the typical catalytic performance of  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -CP and  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -SG in the oxidative dehydrogenation of n-butene at 420 °C after a 6 h-reaction. Selectivity for 1,3-butadiene over both catalysts was almost the same, while conversion of n-butene over  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -SG catalyst was much higher than that over  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -CP catalyst. As a consequence, the  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -SG catalyst exhibited a higher yield for 1,3-butadiene than the  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -CP catalyst. This indicates that the

citric acid-derived sol-gel method was more efficient than the co-precipitation method in the preparation of  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$  catalyst for the oxidative dehydrogenation of n-butene.

Oxidative dehydrogenation of n-butene in the absence of oxygen feed and n-butene-TPD experiments were conducted over both catalysts, in order to elucidate their different catalytic performance. Oxidative dehydrogenation of n-butene in the absence of oxygen feed revealed that the  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -SG catalyst retained a larger oxygen capacity (the amount of oxygen in the catalyst consumed for the oxidative dehydrogenation of n-butene to 1,3-butadiene) than the  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -CP catalyst. In the n-butene-TPD experiments, it was also found that the  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -SG catalyst retained more abundant adsorption sites for n-butene than the  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -CP catalyst. Therefore, it is concluded that the enhanced catalytic performance of  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -SG was attributed to its abundant oxygen species for the reaction and sufficient adsorption sites for n-butene on the catalyst surface.

## Significance

Developing an efficient multicomponent bismuth molybdate catalyst for the production of 1,3-butadiene from  $\text{C}_4$  raffinate-3 feed would be of great interest in an industrial viewpoint.



**Figure 1.** Catalytic performance of  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -CP and  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$ -SG in the oxidative dehydrogenation of n-butene to 1,3-butadiene at 420 °C after a 6 h-reaction.

## References

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