Co-feeding effect of H_2S on propane dehydrogenation performance of transition metal (Fe, Co, Ni) catalysts

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Abstract: The aim of this study was to develop a novel route for a propylene production by a transition metal (Fe, Co, Ni) catalyst via propane dehydrogenation (PDH) with co-feeding hydrogen sulfide (H_2S). The silica supported iron oxide catalyst modified by sulfate ion (Fe-SO_4^{2-}/SiO_2) showed a high propane conversion with an excellent selectivity to propylene. Comparing to the propylene yield over the Cr/Al_2O_3 catalyst, the Fe-SO_4^{2-}/SiO_2 catalyst displayed a better stability for 200 min.

Keywords: Propane dehydrogenation, Iron oxide, Hydrogen sulfide.

1. Introduction

Propylene is one of the important monomer as intermediate for the production of acrylonitrile, polypropylene and propylene oxide[1,2]. The simple propane dehydrogenation (PDH: (1)) has gained an extensive attention due to a direct production of propylene from economic feed stock of propane[3,4].

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad \Delta H^0 = 124\ \mathrm{kJ{\cdot}mol^{-1}} \qquad (1)$$

The alumina supported chromium oxide catalyst (Cr/Al_2O_3) is known to show an excellent performance for PDH. However, a severe coke deposition occurs during the reaction, and the deposited coke deactivates the dehydrogenation activity in short reaction period. Thus, a coke elimination process is required to regenerate the catalytic performance[5]. For these reasons, a novel catalyst is desired to develop for a continuously production of propylene.

In a previous study, we found that the transition metal (Co, Fe) catalyst loaded on an alumina substrate, which included sulfate ion (SO_4^{2-}), indicated a selective performance for PDH[6]. The loaded sulfate ion (SO_4^{2-}) was reduced to the sulfide ion (S^{2-}) among the dehydrogenation reaction, which worked as the active site for the PDH. In this study, in order to promote the formation of sulfide ion (S^{2-}) on the catalyst, hydrogen sulfide (H_2S) was co-fed to the catalyst with propane, and then a catalytic performance over the transition based catalyst for PDH with H_2S was evaluated.

2. Experimental

Transition metal (Fe, Co, Ni) and sulfate ion (SO_4^{2-}) were loaded by co-impregnation method. The γ-Al_2O_3 (JRC-ALO8), SiO_2 (JRC-SIO4), ZrO_2 (JRC-ZRO3), CeO_2 (JRC-CEO2) and MgO (JRC-MGO4) were used as the catalyst support. Each transition metal nitrate and ammonium sulfate were loaded on these supports by co-impregnation method, and followed by an evaporation to dryness. After a calcination of the catalyst at 700ºC for 1 h under air atmosphere, the sulfated catalyst was obtained (abbreviated as M-SO_4^{2-}/support, M: Fe, Co, Ni, support: Al_2O_3, SiO_2, ZrO_2, CeO_2, MgO). The Al_2O_3 supported chromium oxide (Cr/Al_2O_3) catalyst was also prepared by impregnation method to compare the catalytic performance. After a calcination of the catalyst at 700ºC for 1 h under air atmosphere, the Cr/Al_2O_3 catalyst was obtained. The loading amount of transition metal species and SO_4^{2-} species were 20 wt% and 5 wt%, respectively.

The activity test was performed using a conventional fixed bed reactor at atmospheric pressure. The catalyst was placed in the center of the reactor. Before the reaction, the catalyst was reduced by H_2/He = 2.5/47.5 $\mathrm{ml{\cdot}min^{-1}}$ stream at 600°C for 1 h. After that, the reactant gases of C_3H_8, H_2S and He were supplied to the reactor by 2.5 $\mathrm{ml{\cdot}min^{-1}}$, 3.5 $\mathrm{ml{\cdot}min^{-1}}$ and 20 $\mathrm{ml{\cdot}min^{-1}}$, respectively. The reaction temperature was 600°C, and reaction time was 200 min.

3. Results and discussion

Figure 1(a) shows propane conversion over the Fe-SO_4^{2-}/support (support: Al_2O_3, SiO_2, ZrO_2, ZeO_2, MgO) catalysts for PDH in the presence of H_2S. The Fe-SO_4^{2-}/Al_2O_3 and Fe-SO_4^{2-}/SiO_2 catalysts displayed a high propane conversion. In addition, the Fe-SO_4^{2-}/SiO_2 catalyst also showed a high stability for 200 min. Other catalysts showed a low activity and stability. The Co-SO_4^{2-}/support and Ni-SO_4^{2-}/support catalysts exhibited a similar performance for PDH with H_2S (not shown). Among these transition metal catalysts, the Fe-SO_4^{2-}/SiO_2 catalyst showed the highest dehydrogenation performance. The products selectivity at 200 min is shown in Figure 1(b). From this figure, Fe-SO_4^{2-}/SiO_2 displayed the highest propylene selectivity of 92.8 %. The propylene selectivity of the other catalysts was as follows: 82.7 % over the Fe-SO_4^{2-}/Al_2O_3; 74.5 % over the Fe-SO_4^{2-}/ZrO_2; 73.0 % over the Fe-SO_4^{2-}/Al_2O_3; and 67.3 % over the Fe-SO_4^{2-}/CeO_2. By-products of ethylene and methane were produced by decomposition of propane ($C_3H_8 \rightarrow CH_4 + C_2H_4$) and/or hydrogenolysis reaction of propylene ($C_3H_6 + H_2 \rightarrow CH_4 + C_2H_4$). Propane dehydrogenation performance and product selectivity largely depended on the kind of catalyst support.

Figure 2 shows propylene yield over the Fe-SO_4^{2-}/SiO_2 catalyst and Cr/Al_2O_3 catalyst, which was known as the high performance for PDH. The dehydrogenation performance over the Cr/Al_2O_3 catalyst was evaluated under PDH with or without H_2S. The Cr/Al_2O_3 catalyst showed a high propylene yield at initial stage of reaction, but immediately deactivated with reaction time even when H_2S was present in the dehydrogenation atmosphere. The stability and propylene selectivity of Fe-SO_4^{2-}/SiO_2 catalyst were superior to Cr/Al_2O_3. From these result, the Fe-SO_4^{2-}/SiO_2 catalyst was considered to be one of the effective catalysts for PDH with H_2S.

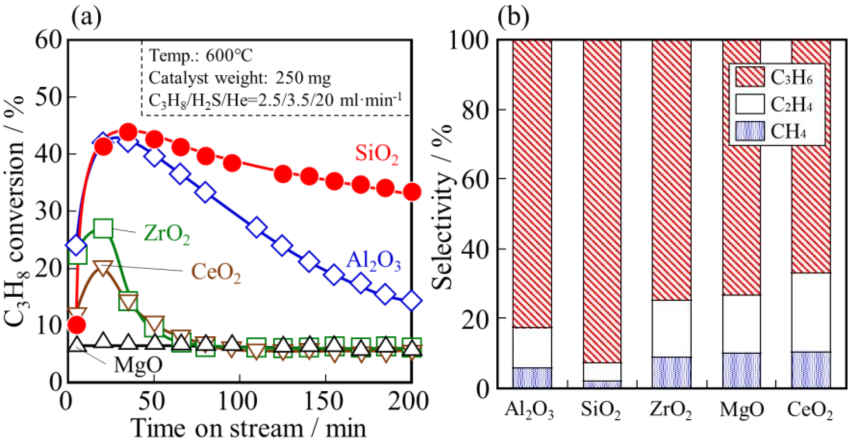

Figure 1 (a) C_3H_8 conversion and (b) products selectivity at 200 min over Fe-SO_4^{2-}/support (support: Al_2O_3, SiO_2, ZrO_2, CeO_2, MgO) catalysts.

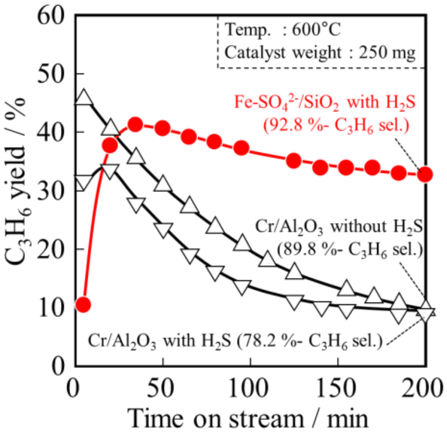

Figure 2. Comparison of C_3H_6 yield over the Fe-SO_4^{2-}/SiO_2 and Cr/Al_2O_3 catalysts.

4. Conclusions

The Fe-SO_4^{2-}/Al_2O_3 and Fe-SO_4^{2-}/SiO_2 catalysts displayed a high dehydrogenation performance for PDH in the presence of H_2S. The Fe-SO_4^{2-}/SiO_2 catalyst displayed the highest propylene selectivity and good stability among transition metal (Fe, Co, Ni) catalysts during the PDH reaction. The dehydrogenation performance was largely depended on the supports. Comparing to the propylene yield over the Cr/Al_2O_3 catalyst, the Fe-SO_4^{2-}/SiO_2 catalyst showed a higher selectivity and better stability.

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