The Inhibition Effect of Potassium Addition on Methane Formation in Steam Reforming of Acetic Acid over Alumina-supported Cobalt Catalysts

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The inhibition effect of potassium addition on methane formation in steam reforming of acetic acid over alumina-supported cobalt catalyst has been studied. Co–K/Al_2O_3 catalyst showed much higher activity for hydrogen generation and much lower selectivity for methane than Co/Al_2O_3. Potassium addition resulted in the inhibition of methanation process. The similar effect was also observed in methanol and ethanol reforming reactions.

Currently renewable source to hydrogen is a very attractive topic owing to the fast depletion of fossil fuel.[1] In general, biooil is a complex mixture of organic compounds including many organic acids.[2] Acetic acid is one of the main components in biooil.[3] In addition, acetic acid is nonflammable; therefore, it is a safe hydrogen carrier. Steam reforming of acetic acid always gave significant amount of by-products such as methane, which resulted in low hydrogen yield.[4] Methane formation is highly dependent on the amount and the density of acidic centers on catalyst support,[5,6] neutralization of acidic center by basic species may lead to the significant variation of catalyst ability of inhibiting methane formation. In this paper, potassium was added to the support to modify the properties of alumina support. Comparing studies on Co/Al_2O_3 and Co–K/Al_2O_3 catalysts, the remarkable inhibition effect of potassium on methane formation was found.

Co/Al_2O_3 was prepared by impregnation method using $Co(NO_3)_2 \cdot 6\,H_2O$ as a precursor. The cobalt loading was 30 wt % to Al_2O_3. Before impregnation, the support γ-Al_2O_3 (129 m^2/g, 30–45 mesh) was stabilized in air at 600 °C for 6 h. After impregnation, the catalyst precursor was dried at room temperature for 24 h and at 110 °C for another 24 h. Finally, the catalyst precursor was calcined at 500 °C for 4 h. Co–K/Al_2O_3 was prepared by coimpregnation method using a mixed solution containing both $Co(NO_3)_2$ and KNO_3. Potassium loading amount was 8 wt %.

Catalytic tests were carried out in a fixed bed continuous flow quartz reactor at atmospheric pressure. Typically, 0.5 g of catalyst diluted with equal amount of quartz was reduced at 600 °C for 3 h in situ with a 50 vol % H_2/N_2 mixture (flow rate: 60 mL/min) prior to experiment. The reaction mixture was fed into a preheater by a syringe pump with a liquid hourly space velocity (LHSV) of 10.1 h^{-1} under steam to carbon ratio (S/C) of 7.5:1. Product was analyzed by two on-line chromatographs equipped with a thermal-conductivity detector (TCD) and a flame ionization detector (FID). H_2 selectivity was defined as the fraction of H_2 produced with respect to the H_2 of theoretical datum of full conversion of acetic acid ($CH_3COOH + 2H_2O \rightarrow 4H_2 + 2CO_2$). Selectivity to methane was defined by the formula: S_{CH_4} (%) $= 100 \times$ (mole of CH_4 generated)/(mole of acetic acid consumed $\times$ 2). The selectivities to others were calculated in the similar way. Temperature-programmed reduction analysis (H_2-TPR) was carried out by heating a sample (30 mg) in a flow of 5 vol % H_2/Ar mixture (40 mL/min).

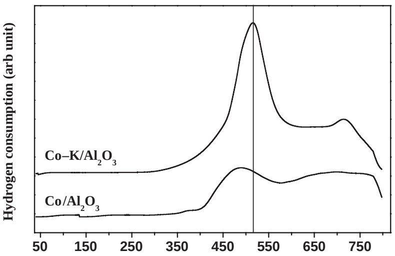

Figure 1. H_2-TPR profiles for bare and modified Co catalysts.

Results of H_2-TPR for Co/Al_2O_3 and Co–K/Al_2O_3 catalysts were shown in Figure 1. The addition of potassium induced a shift of the main reduction peak of cobalt oxide upwards to higher temperature. However, the H_2 uptake for Co–K/Al_2O_3 was much higher than that of Co/Al_2O_3. Higher H_2 uptake implied existence of more reducible Co species on catalyst surface, which was active for steam-reforming reaction.[7] It was reported that potassium could lead to alumina carrier passivated and became less reactive.[8] Therefore, potassium addition resulted in the significant enhancement of cobalt oxide reducibility in Co–K/Al_2O_3.

The catalytic properties of Co/Al_2O_3 and Co–K/Al_2O_3 were examined in the temperature region of 300–600 °C. Complete conversion of acetic acid was achieved above 450 °C over Co/Al_2O_3, the corresponding H_2 selectivity was 80%. Below 450 °C, the activity of Co/Al_2O_3 was quite low. Pronounced amount of by-products such as methane, CO, acetone, and ketene were formed, which resulted in low H_2 yield. The catalytic performance of Co/Al_2O_3 can be significantly improved by the potassium addition at 350 °C, as presented in Figure 2. Acetic acid was converted completely even at temperature of 350 °C over Co–K/Al_2O_3. Besides, much higher H_2 selectivity (93.5%) was obtained at 350 °C. The productions of the by-products were also remarkably suppressed compared to Co/Al_2O_3 catalyst. Very interestingly, only trace amount of methane was found over Co–K/Al_2O_3 at 350 °C. Moreover, in the whole range of tested temperature, much lower methane selectivity was achieved over Co–K/Al_2O_3 (as shown in Figure 3). Since production of 1 mol of methane will consume 1 mol of acetic acid and result in loss of 4 mol of hydrogen in acetic acid reforming reaction, the suppression of methane formation is very important in enhancement of hydrogen yield.

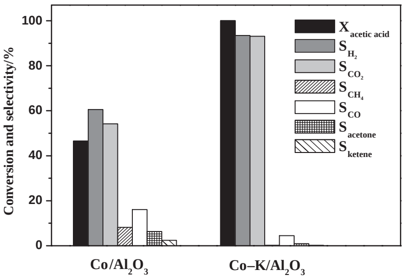

Figure 2. Acetic acid conversion and product selectivity at 350 °C over Co/Al_2O_3 and Co–K/Al_2O_3.

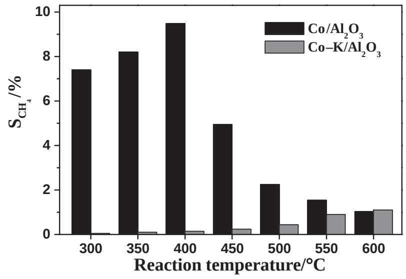

Figure 3. CH_4 selectivity vs. reaction temperature over Co/Al_2O_3 and Co–K/Al_2O_3.

In acetic acid reforming process, acetic acid decomposition may occur according to the following way: $CH_3COOH \rightarrow CH_4 + CO_2$. In addition, methanation of carbon oxides may lead to methane formation,[9] while the steam reforming of methane may decrease the detected amount of methane. However, our blank tests indicated that both catalysts exhibited very low activity for methane steam reforming at temperature below 600 °C; therefore, steam reforming of methane was not considered in this study.

For proving decomposition reaction hypothesis, we carried out an acetic acid decomposition experiment using pure acetic acid with a LHSV of $5.0\,h^{-1}$ at 400 °C. Co–K/Al_2O_3 gave a similar acetic acid conversion and methane selectivity to Co/Al_2O_3 catalyst. Evidently, acetic acid decomposition was not the main reason for the low CH_4 selectivity over Co–K/Al_2O_3. The methane formation was probably inhibited by potassium in reforming reaction. Thus, the methanation reaction was subsequently conducted in the temperature region of 300–600 °C using two reactors. Acetic acid was firstly reformed with steam in the first reactor to generate the effluent gas, which was then introduced into the second reactor to measure the methanation activity of the catalysts. The results were given in Figure 4. Co/Al_2O_3 showed higher methanation activity, while the methanation activity of Co–K/Al_2O_3 was much lower, especially at middle temperatures. These results matched well with the lower methane selectivity over Co–K/Al_2O_3 in steam-reforming process, as presented in Figure 3. Therefore, it was believed that the low methanation activity of Co–K/Al_2O_3 was the main reason for its low methane selectivity in the reforming process.

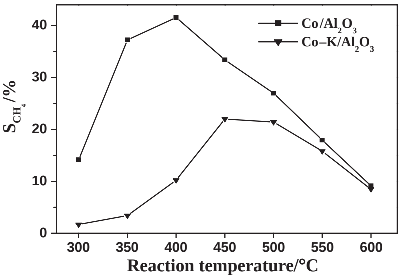

Figure 4. Methanation reactions over Co/Al_2O_3 and Co–K/Al_2O_3.

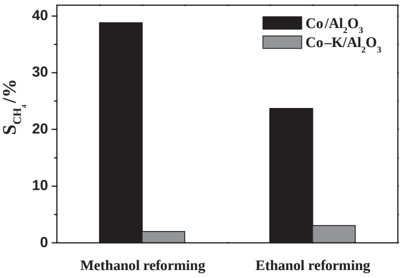

Figure 5. CH_4 selectivity in methanol- or ethanol-reforming reactions over Co/Al_2O_3 and Co–K/Al_2O_3.

The effect of potassium on the generation of methane in methanol- or ethanol-reforming reactions was also studied under the similar conditions. As shown in Figure 5, the selectivity for methane was significantly lower in both methanol- and ethanol-reforming reactions over Co–K/Al_2O_3 than over Co/Al_2O_3 at 400 °C.

To the conclusion, potassium could promote the reduction of cobalt oxide, resulting in the remarkable increase of the low-temperature reforming activity of Co/Al_2O_3. The production of methane in steam reforming of acetic acid, methanol, and ethanol could be significantly reduced with potassium addition to Co/Al_2O_3 because of the inhibition effects of potassium on the methanation reactions.

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