Formic Acid Decomposition for Hydrogen Production over Molybdenum Based Catalyst Supported on Lignin-derived Carbons

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Abstract: In this work, alkaline lignin (AL), dealkaline lignin (DAL), and activated carbon (AC) were used as the carbon source to prepare molybdenum based catalysts. The effect of the carbon source on the catalytic decomposition of formic acid was investigated. It is found that the catalyst prepared by using DAL as the carbon source showed the highest catalytic activity. When the 5% Mo-DAL was used, formic acid was completely converted with a low CO/H_2 mol ratio of 0.007 at 250 °C. In addition, the catalyst exhibited stable activity for at least 50 h in this condition.

Keywords: Formic acid decomposition, Molybdenum based catalyst, Lignin utilization.

1. Introduction

Formic acid has a potential to be used as an on-site hydrogen source for fuel cells since it is easy to be stored and transported [1]. In order to achieve practical application of formic acid as a hydrogen carrier, it is inevitable to develop cheap, namely, non-precious metal catalysts. In this view point, molybdenum carbide is an attractive catalyst material. To date, three main routes have been applied to synthesize this material: solid-gas, solid-liquid, and solid-solid reactions. Among them, the solid-solid synthesis route is more beneficial since it is relatively simpler and safer than others [2].

Lignin is considered as an abundant carbon source, which is mainly produced in pulp and paper industries as waste. In this study, two kinds of lignin (Alkaline (AL) and dealkaline lignin (DAL)), and activated carbon (AC) were used as the carbon sources and catalyst supports for producing molybdenum based catalysts. The obtained catalysts were applied for the formic acid decomposition and the effect of carbon source on the reaction was investigated. It is found that the decomposition mainly occurred in the H_2-CO_2 route where only a little amount of carbon monoxide was produced as the byproduct.

2. Experimental

AL and DAL were provided from Tokyo Chemical Industry Co., Ltd. (TCI). Activated carbon (0.2-1 mm) was purchased from Wako Pure Chemical Industries, Ltd. Ammonium heptamolybdate pentahydrate (Wako, Japan) was used as a molybdenum source. After impregnating the molybdenum source on the carbon sources by impregnation method, the obtained precursors were dried at 110 °C in the oven overnight, followed by grinding, carbonization at 800 °C under an argon gas flow, and passivation in 1% O_2/Ar for 12 h at room temperature. The prepared catalysts were characterized by XRD, SEM-EDX and FT-IR.

Catalytic performances were evaluated in a quartz fixed bed micro-reactor at the temperature range from 150 to 350 °C. Firstly, 0.25 g of a catalyst packed in the reactor was activated by 15% CH_4/H_2 at 600 °C for 2 h prior to the formic acid decomposition. Then, formic acid (WHSV of 4 h^{-1}), which was pre-vaporizaed at 120 °C, was carried by 60 cm^3/min of argon flow to the catalyst bed. The gaseous products were analyzed by GC-TCD to determine the conversion of formic acid and CO/H_2 mol ratio.

3. Results and discussion

Catalytic decompositions of formic acid were performed at 150-350 °C. Table 1 compares the best catalytic performances of the catalysts prepared by using AL, DAL and AC as the carbon sources with a 20 wt.% loading amount of molybdenum. One can see that 20% Mo-DAL resulted in the highest conversion with a lower mol ratio of CO/H_2 at a lower temperature than 20% Mo-AL at the best condition. Furthermore, when compared with 20% Mo-AC, the 20% Mo-DAL also resulted in a lower mol ratio of CO/H_2. These results indicate that the catalyst prepared by using DAL exhibited the highest catalytic activity.

The effect of Mo loading amount on the catalyst performance of Mo-DAL was also investigated. In the case of 5 wt.% Mo loading amount, formic acid was completely converted with a low CO/H_2 mol ratio of 0.007 at 250 °C. Furthermore, Figure 2 shows the 5% Mo-DAL catalyst exhibited a highly stable activity for at least 50 h in the best operation condition. Although WHSV was changed to 8 h^{-1} from $4h^{-1}$, the average conversion of formic acid still maintained at 91%.

Figure 3 shows XRD patterns of fresh and spent 5% Mo-DAL at each step of reaction. Intense peaks ascribable to Na_2S were observed on the XRD pattern of 5% Mo-DAL after the activation process, indicating that sodium sulfate containing in DAL was converted into this material under the reductive condition. Moreover, the peaks ascribable to sodium formate and sodium intercalated molybdenum sulfide were found after the reaction. Observation of those species suggests that sodium species which may work as absorption sites of formic acid and sulfide species which may work as enhancer improved the catalytic activity of molybdenum based catalysts. Therefore, DAL should be the best carbon source and catalyst support among the applied carbon sources.

Table 1. The best catalytic performances of lignin based Mo catalysts

Catalyst	20% Mo-AC	20% Mo-AL	20% Mo-DAL	10% Mo-DAL	5% Mo-DAL	1% Mo-DAL	DAL
Temperature (°C)	250	350	250	250	250	300	350
Conversion (%)	100	100	100	100	100	100	77.2
CO/H_2 mol ratio	0.048	0.213	0.009	0.009	0.007	0.023	0.410

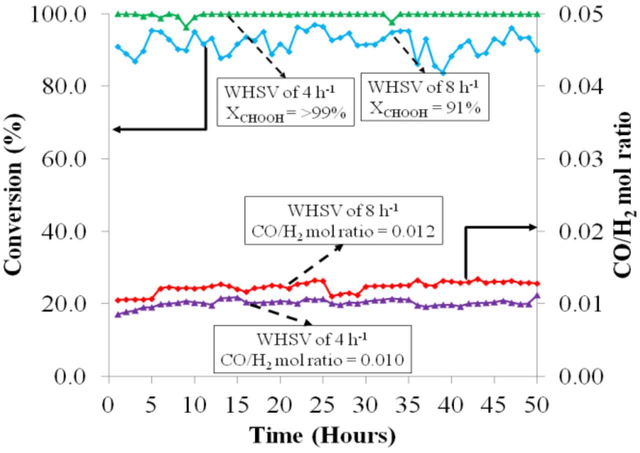

Figure 2. Stability test of 5%Mo-DAL with different WHSV conditions.

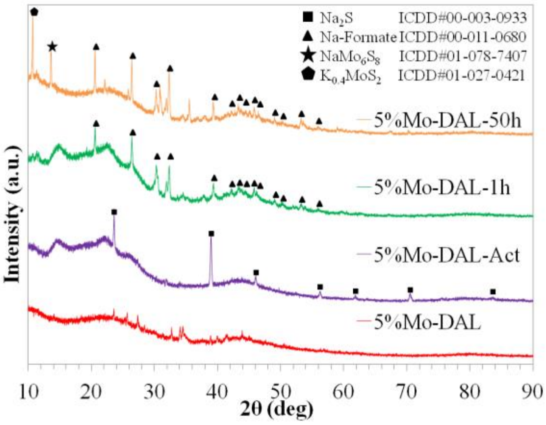

Figure 3. XRD patterns of fresh and spent 5% Mo-DAL catalysts.

4. Conclusions

The molybdenum based catalysts were prepared by using lignin as the carbon source for the catalytic decomposition of formic acid for hydrogen production. The 5% Mo-DAL catalyst showed high and stable activity at 250 °C. Sodium and sulfur containing in DAL probably worked as enhancers to improve the catalytic activity of the DAL based catalysts.

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