Direct Dehydrogenative Conversion of Methane into Higher Hydrocarbons through Liquid-Metal Indium Catalyst

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Abstract: Dehydrogenative conversion of methane (DCM) is an attractive reaction. We already reported that liquid-metal indium supported on silica (In/SiO_2) was an effective catalyst for DCM. Characterization studies and kinetic studies indicated that liquid-metal indium catalyzed cleavage of a C-H bond of methane and coupling methane to ethane selectively. In addition, conversion of ethane and temperature-programmed reaction in ethane (TPR-C_2H_6) suggested that indium did not activate both a C-H bond and a C-C bond of ethane. Indium has the unique catalysis to activate only a C-H bond of methane, therefore, selectivity to hydrocarbons was still high despite high temperature.

Keywords: Methane conversion, Liquid metal catalysis, Indium catalysis.

1. Introduction

Methane (CH_4) is the main component of natural gas, which is an abundant energy sources in the earth. Most of CH_4 is currently used to generate electric power and heat because it is difficult to convert CH_4 to valuable compounds. Steam reforming of CH_4 to syngas (CO + H_2) and following catalytic reactions are only realized as industrial processes for utilization of CH_4. These processes need large amount of energy and costs because of mult-step reaction. Therefore, direct conversion of methane to chemicals and liquid fuels is a promising way to utilize natural gas.

In dehydrogenative conversion of CH_4, molybdenum/zeolite (Mo/zeolite) catalysts have been extensively studied and tested to overcome coke deposition[1,2]. Recently, a few new DCM catalysts were reported. For example, Guo et al. reported the Fe/SiO_2 catalyst (single Fe sites in a silica matrix) to convert CH_4 to ethylene, benzene and naphthalene at >1223 K[3]. We also reported the In/SiO_2 catalyst to convert CH_4 to ethylene, propylene and benzene[4]. CH_4 conversion was 4.8% and selectivity to hydrocarbons was 75 % by the In/SiO_2 catalyst at 1173 K. In this work, we study detailed reaction mechanisms for the DCM reaction on the In/SiO_2 catalyst.

2. Experimental

The In/SiO_2 catalyst was prepared by a conventional impregnation method. Indium nitrate hydrate was dissolved in deionized water and CARiACT Q-3 (SiO_2 support) was added to the solution. The mixture was dried up at 393 K. This catalyst precursor was calcined at 773 K in air and was reduced with H_2 at 873 K. The DCM reaction tests were conducted using a fixed-bed quartz reactor (I.D. 12 mm) with In/SiO_2 (100 mg) and CH_4 (1 atm, 10 mL min^{-1}) was flowed. Hydrocarbons and H_2 were analyzed by gas chromatographs or an online mass spectrometer. In the cases of conversion of C_2H_6, 5% C_2H_6/Ar (1 atm, 30 mL min^{-1}) or 0.5% C_2H_6/H_2 (1 atm, 20 mL min^{-1}) was flowed. A Ni/SiO_2 catalyst as a reference one was prepared from nickel nitrate hexahydrate using the same method.

3. Results and discussion

Figure 1 (a)-(d) show the profiles of temperature-programmed reaction (TPR) from 323 K to 1173 K with 4 K min^{-1} monitored by a mass spectrometer. In the TPR using CH_4 on In/SiO_2 (a), formation of C_2H_6 (m/z = 30) was observed from 800 K. On the other hand, no formation of C_2H_6 on SiO_2 (b).It was clear that indium catalyzed CH_4 activation and propylene and benzene were successively produced following the C_2H_6 formation. In the TPR using C_2H_6 on In/SiO_2 (c), significant products were not detected at 800 K. Formations of H_2 (m/z = 2) and CH_4 (m/z =16) were observed over 950 K, corresponding to conversion of C_2H_6 (m/z = 28, 30). In the case of SiO_2 (d), similar profiles were observed except for hydrogen production which was slightly suppressed by In/SiO_2. Figure 1 indicated that indium could activate a C-H bond of CH_4, however, a C-H bond of C_2H_6 cannot.

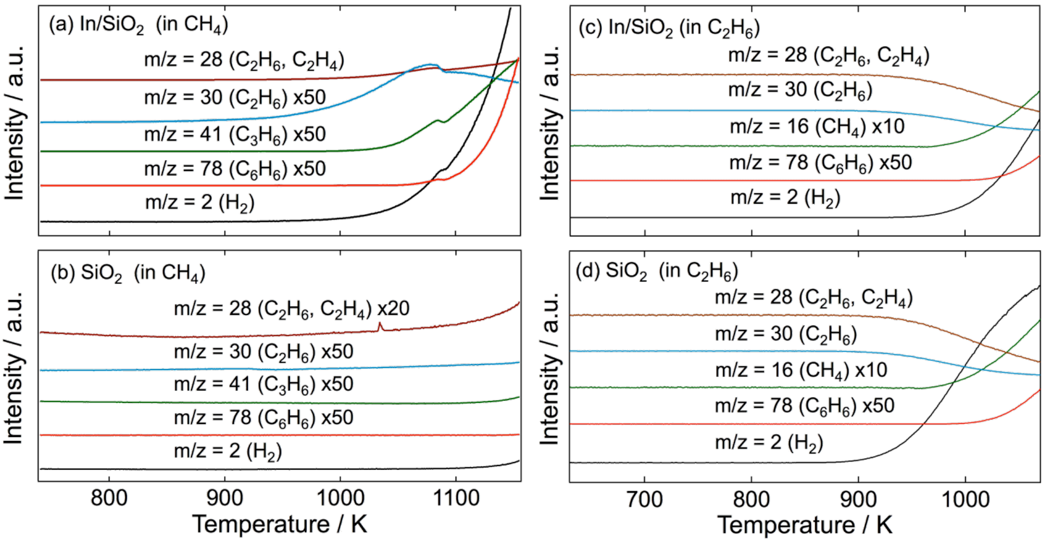

Figure 1. Mass spectra of temperature-programmed reaction in CH_4 over (a) SiO_2 and (b) In/SiO_2 and in C_2H_6 by (c) SiO_2 and (d) In/SiO_2 with 4 K min^{-1}.

To obtain more information of indium catalysis, conversion of C_2H_6 in H_2 was conducted. As references, results of no catalyst and Ni/SiO_2 catalyst were shown in Table 1. Ni/SiO_2 catalyst converted C_2H_6 into CH_4 and coke, therefore, a C-C bond of C_2H_6 was cleaved. On the other hand, dehydrogenation of C_2H_6 to C_2H_4 was mainly proceeded on In/SiO_2.
The selectivities on In/SiO_2 were very similar to that of no catalyst. This indicated that distributions were thermodynamically decided. Indium cannot activate C-H and C-C bonds of C_2H_6, therefore, carbon deposition was suppressed. In the presentation, DFT-calculation results will be discussed.

Catalyst	C_2H_6 conv. / %	Selectivity / %		
		CH_4	C_2H_4	Coke
Ni/SiO_2	91	67	8	25
In/SiO_2	58	18	76	6
None	61	21	67	12

Table 1. C_2H_6 conversion in H_2 over Ni/SiO_2, In/SiO_2 and no catalyst at 1073 K.

4. Conclusions

Results of TPR-CH_4 and TPR-C_2H_6 on In/SiO_2 indicated that indium could activate only a C-H bond of CH_4 but not a C-H bond of C_2H_6. Additionally, indium cannot cleave a C-C bond of C_2H_6 from the results of conversion of C_2H_6. These unique catalysis of In/SiO_2 for CH_4 and C_2H_6 results in higher selectivity to hydrocarbons in the DCM reaction.

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