

Supporting Information

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Experimental section

Catalysis of In on supports was studied for the DCM reaction. Indium (10 wt%) loaded on support (10wt% In/support) catalysts were prepared by a conventional impregnation method and reduction with H₂. In the case of SiO₂, CARiACT Q-3 support was calcined in air at 1273 K, which surface area was very low as 0.05 m² g⁻¹. The 10wt% In/SiO₂ catalysts have almost the same surface area of 0.05 m² g⁻¹. The DCM reaction was conducted using a conventional fixed-bed gas-flow system and a quartz tube reactor (I.D.: 12 mm). Pure dry CH₄ with 10 mL(STP) min⁻¹ passed through the catalyst (100 mg) bed at 723-873 K for 2 h. Products were analyzed using gas chromatographic techniques. Experimental procedures in details and calculation methods for product yields and selectivity are indicted below.

In/SiO₂

In(NO₃)₃·nH₂O was added to deionized water and the calcined CARiACT Q-3 was added to the solution. The mixture was dried up at 353 K under stirring. The precursor was calcined at 393 K for 2 h and at 773 K for 3 h. The calcined powder was reduced with H₂ at 873 K for 3 h. Metal loading of the In/SiO₂ catalysts is 10wt%.

Procedure of experiment

We showed typical handling of the DCM reaction as below. As shown in Figure S1, catalyst (100 mg) was set in a fixed-bed quartz reactor (inner diameter of 12 mm) and CH₄ (1 atm, 10 mL min⁻¹) was introduced into the reactor at 873 K. Products of hydrocarbons and H₂ were analyzed by gas chromatograph techniques every half hour. H₂ was quantified by a gas chromatograph (Shimadzu, GC-8A-TCD, active carbon column (3 mm, 2 m)). CH₄, C₂H₆, C₂H₄ were quantified by a gas chromatograph (Shimadzu, GC-8A-FID, Unibeads-1S column (3 mm, 2 m)).

Reagents and materials

In(NO₃)₃·nH₂O (99.99% trace metal basis) is purchased from Sigma Aldrich. Silica support of CARiACT Q-3, CARiACT Q-30, Admafine SO-E6, AEROSIL 3000 are purchased from Fuji Silysia Chemical Company. Molecular sieve 3A and 4A, other reagents used in this work were special grade and were purchased from Wako Pure Chemical Industries. All chemicals were used without farther purification.

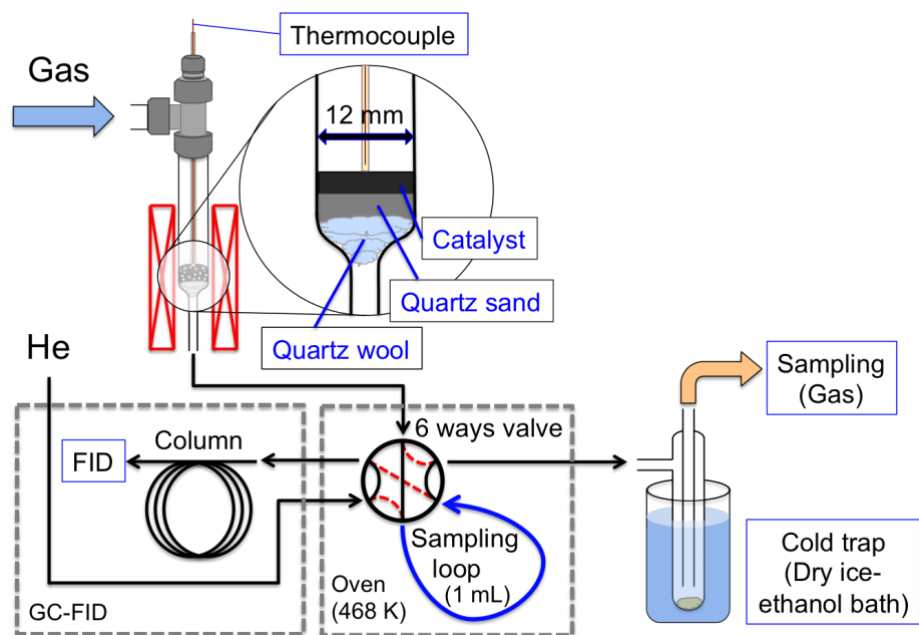


Figure S1. The apparatus for the DCM reaction and the dehydrogenation of C_2H_6 and C_2H_4 .

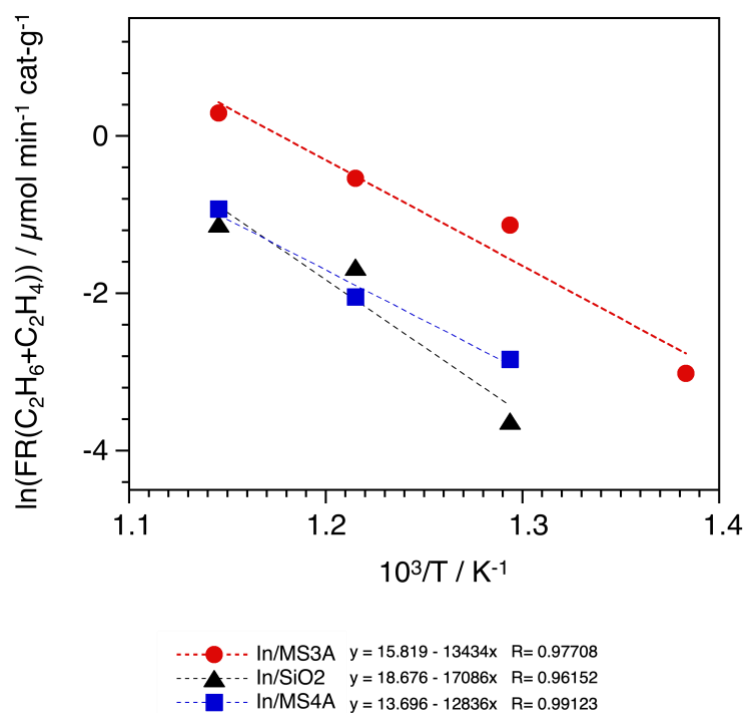


Figure S2. Arrhenius plot of the DCM reaction over In/MS3A(humid), In/MS4A(humid) and In/SiO₂ (humid) catalysts. Replot of Figure 4 in the main text.