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Supplementary Information

Methane Conversion on Cobalt-Added Liquid-Metal Indium Catalysts

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Experimental

Preparation of catalysts

All catalysts were prepared by a typical impregnation method. $In(NO_3)_3 \cdot nH_2O$ (Sigma-Aldrich), $Co(NO_3)_2 \cdot 6H_2O$ (Kanto Chemical Co., Inc.), and SiO_2 (CABOT; CAB-O-SIL M-5 Fumed Silica) were added to deionized water (50 mL), and heated on a hot plate under stirring. The obtained powder was calcined at 1073 K in air. Loading of In was 5 wt% in all catalysts. The loading of Co in Co/SiO_2 was 0.5 wt%. In-Co/SiO_2 catalysts with 1, 2, 9, 17, 50 atomic% of Co were prepared, and denoted as In-Co(1), In-Co(2), In-Co(9), In-Co(17), and In-Co(50)/SiO_2, respectively. The Co loadings for In-Co(1), In-Co(2), In-Co(9), In-Co(17), and In-Co(50)/SiO_2 were 0.026, 0.051, 0.26, 0.51, and 2.6 wt%, respectively.

CH_4 conversion reaction

CH_4 conversion reactions were performed in a fixed-bed reactor. A schematic of the reaction system is shown in Fig. S1. Catalyst (0.20 g) and quartz wool (50 mg) were placed in a quartz reactor. The reactor was purged with Ar flow, and then the catalyst bed was heated to 1073 K. After reducing the catalysts with H_2 at 1073 K, and purging the reactor with Ar, CH_4 (10 mL min^{-1}) was introduced. The CH_4 conversion reaction was carried out for 2 h. In this study, some reactions were carried out repeatedly, and the reproducibility of reaction results was confirmed.

During the reaction, outlet gas of 0.5 mL was injected into gas chromatographs every 15 min. For H_2 and CH_4, a gas chromatograph (Shimadzu GC-8A, TCD) equipped with a packed column (Active carbon) was used at 473 K (injection/detector) and 443 K (column) under flowing Ar as a carrier gas. For C_2 and C_3 hydrocarbons, a gas chromatograph (Shimadzu GC-8A, FID) equipped with a packed column (Unibeads 1S) was used at 453 K (injection/detector) and 383 K (column) under flowing N_2 as a carrier gas. To quantify gaseous products, calibration curves for all products were prepared by injecting different volume of the gases.

Formed aromatics (benzene, toluene, and naphthalene) were collected in a glass trap cooled with a dry ice/ethanol bath. After the reaction, the trapped aromatics were dissolved in acetonitrile and then 30 mM butyl acetate in acetonitrile was added as an internal standard. The obtained solution was injected into a gas chromatograph (Shimazu, GC-18A) equipped with a capillary column (Shinwa chemical industries ltd., ULBON HR-1, 0.25 mm i.d., 30 m) under flowing N_2 as a carrier gas. Temperature for injection/detector was settled at 523 K and temperature for column was raised from 313 K to 473 K at 10 K min^{-1}. To quantify the aromatics, solutions containing different concentration of benzene, toluene, naphthalene, and butyl acetate in acetonitrile were prepared and calibration curves were prepared by injecting the solutions into the GC.

$$CH_4 \rightarrow C + 2H_2 \tag{1}$$

$$2CH_4 \rightarrow C_2H_6 + H_2 \tag{2}$$

$$2CH_4 \rightarrow C_2H_4 + 2H_2 \tag{3}$$

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \tag{4}$$

$$3CH_4 \rightarrow C_3H_8 + 2H_2 \tag{5}$$

$$3CH_4 \rightarrow C_3H_6 + 3H_2 \tag{6}$$

$$6CH_4 \rightarrow C_6H_6 + 9H_2 \tag{7}$$

$$7CH_4 \rightarrow C_7H_8 + 10H_2 \tag{8}$$

$$10CH_4 \rightarrow C_{10}H_8 + 16H_2 \tag{9}$$

In this study, the reaction eqs. 1~9 can take place. Formation rates for gaseous products were estimated using both the GC analysis and flow rates measured with a soap film meter. Total amounts of gaseous products were calculated by integrating formation rates every 15 min. Yields of gaseous products and aromatics were calculated by dividing total amount of products by reaction time. Yield for coke was evaluated from the yields of all products for 2 h using eq. 10.

$$\begin{aligned} Y_{coke} &= 1/2\ (Y_{H2\ \text{detected}} - Y_{H2\ \text{(formed by hydrocarbon formation)}}) \\ &= 1/2(Y_{H2} - Y_{C2H6} - 2Y_{C2H4} - 3Y_{C2H2} - 2Y_{C3H8} - 3Y_{C3H6} - 9Y_{C6H6} - 10Y_{C7H8} - 16Y_{C10H8}) \end{aligned} \tag{10}$$

Ethylene conversion reaction

The catalyst (0.50 g) and quartz wool (15 mg) were placed in a quartz reactor. The reactor was purged with Ar flow, and then the catalyst bed was heated to 1023 K. After reducing the catalysts with H_2 at 1023 K, a mixture of Ar/H_2/ethylene (C_2H_4) (47/3/3 mL min^{-1}) was introduced. The reaction was carried out for 2 h. Analysis procedures for products were the same as in the CH_4 conversion reactions.

Yield for coke was evaluated from the yields of all products using eq. 11.

$$Y_{coke} = Y_{H2} + Y_{CH4} + Y_{C2H6} - 2Y_{C2H2} - 3Y_{C6H6} - 4Y_{C7H8} - 6Y_{10H8} \tag{11}$$

CH_4 and C_2H_4 conversion

CH_4 conversion and C_2H_4 conversion were calculated as follows:

$$CH_4\ \text{conv.} = (r_{coke} + 2r_{C2H6} + 2r_{C2H4} + 2r_{C2H2} + 3r_{C3H8} + 3r_{C3H6} + 6r_{C6H6} + 7r_{C7H8} + 10r_{C10H8}) / r_{CH4,\ inlet} \times 100 \qquad (12)$$

$$C_2H_4\ \text{conv.} = (r_{coke} + r_{CH4} + 2r_{C2H6} + 2r_{C2H2} + 3r_{C3H6} + 6r_{C6H6} + 8r_{C8H8} + 10r_{C10H8}) / (2r_{C2H4,\ inlet}) \times 100 \qquad (13)$$

The conversions shown in Tables 1 and 2 are average values during the reaction.

As described above, we collected formed aromatics in a glass trap cooled with a dry ice/ethanol bath and analyzed them after the reaction. Therefore, when we evaluated time course of conversions (Figs. S2 and S4), we calculated the formation rates of aromatic based on the total amount of them, assuming that formation rates of aromatics were the same during the reaction. The rates for C_2 and C_3 formation were calculated from GC analysis and flow rate measurement every 15 min. The rate of coke formation was calculated using eq. 1, assuming that formation rates of aromatics were the same during the reaction. The rate for CH_4 (inlet) was measured by using a soap film meter prior to the reaction.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded with a D2 phaser (Bruker), using Cu Kα radiation. Field emission scanning electron microscopy (FE-SEM) images were obtained with S-4800 (Hitachi High-Technologies) at 15 kV of accelerating voltage. EDX analysis was carried out using Quantax 400 with XFlash 4010 (Bruker) equipped with the S-4800. Nitrogen adsorption-desorption measurements at 77 K were performed on a Belsorp II (MicrotracBEL) sorption analyzer. Prior to the sorption measurements, the samples were degassed under vacuum at 403 K. Specific surface area was calculated by Brunauer-Emmett-Teller method. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) observation of the catalyst was performed on a JEM-ARM200F-B (JEOL Ltd., Japan) instrument operated at the acceleration voltage of 200 kV.

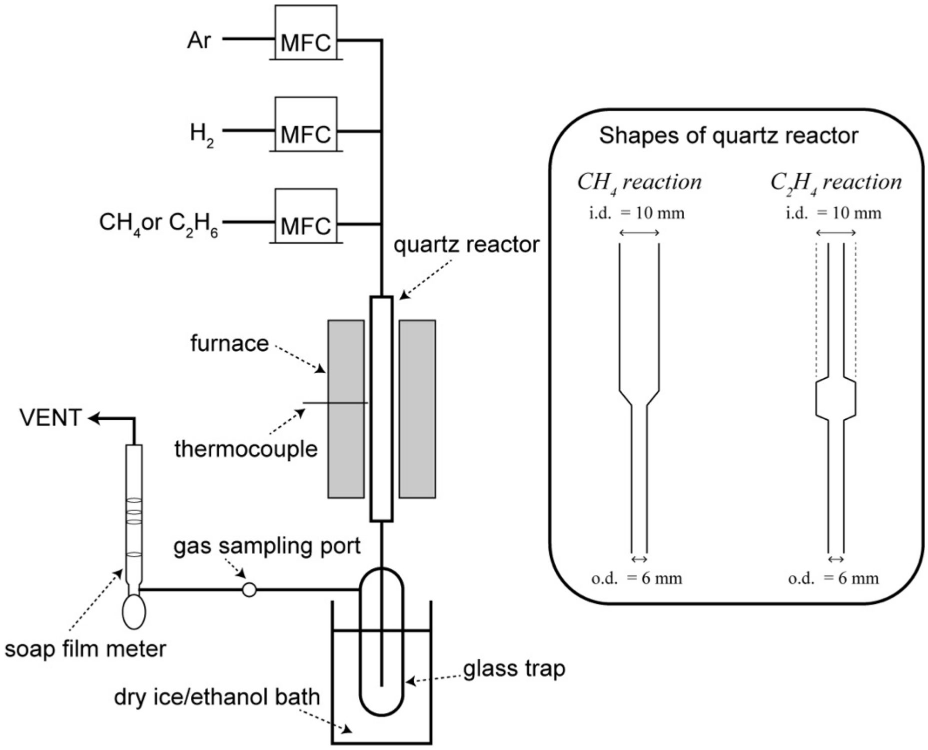

Fig. S1. The schematic diagram of the reaction system in this study.

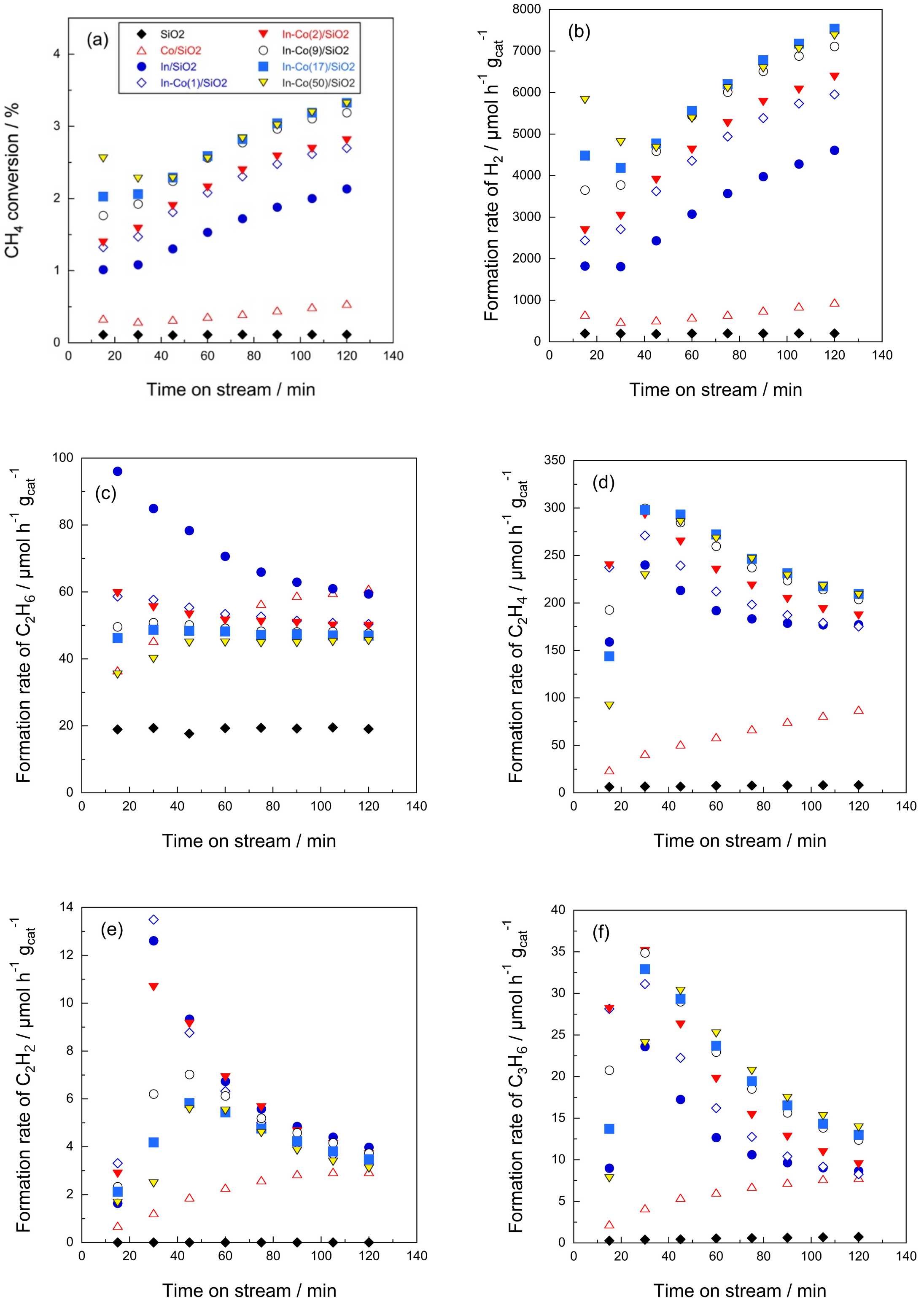

Fig. S2. Time course of dehydrogenative conversion of CH_4 at 1073 K; (a) CH_4 conversion and formation rate of (b) H_2, (c) C_2H_6, (d) C_2H_4, (e) C_2H_2, and (f) C_3H_6.

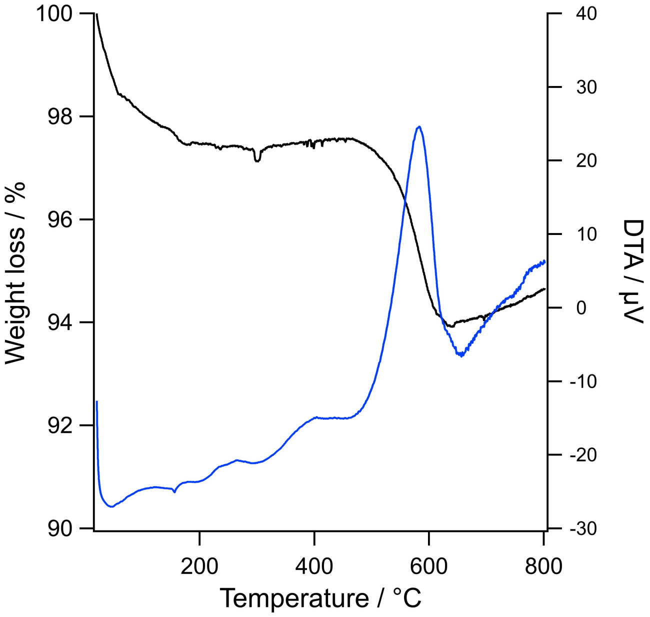

Fig. S3. TG/DTA curves of In-Co(17)/SiO_2 after CH_4 conversion at 1073 K.

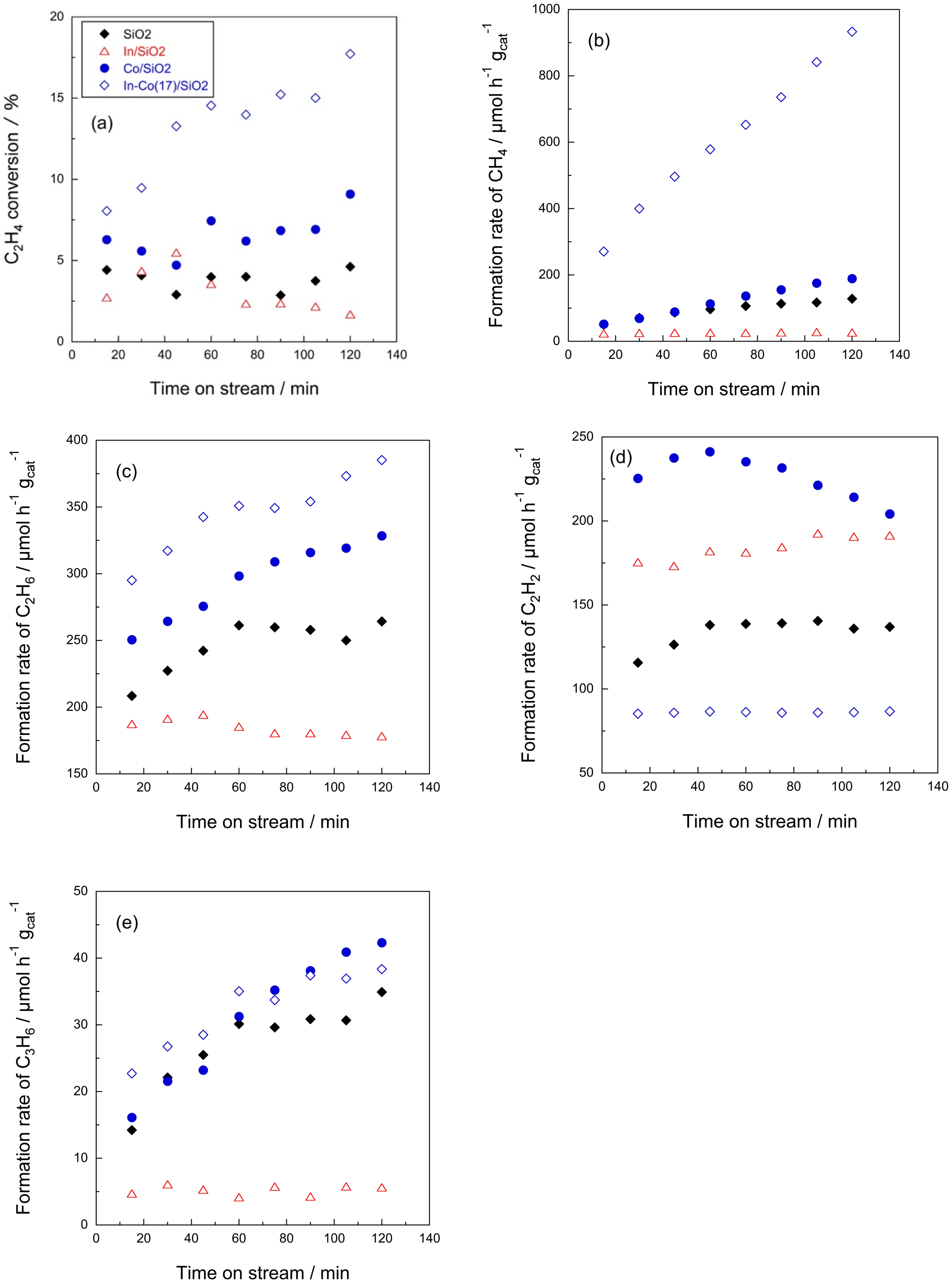

Fig. S4. Time course of conversion of C_2H_4 at 1023 K; (a) C_2H_4 conversion and formation rate of (b) CH_4, (c) C_2H_6, (d) C_2H_2, and (e) C_3H_6.

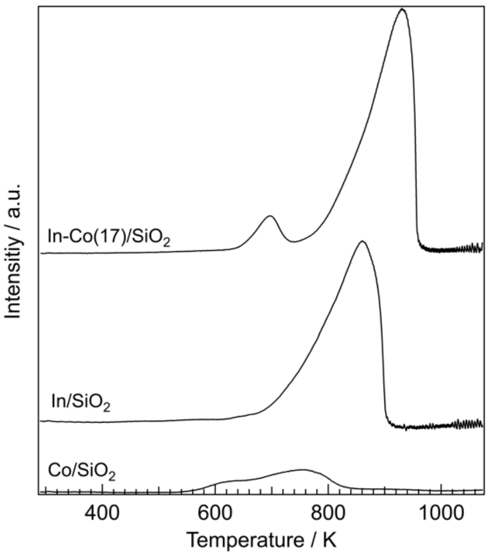

Fig. S5. Temperature programmed reduction (TPR) profiles for In/SiO_2, In-Co(17)/SiO_2, and Co/SiO_2. For the TPR analysis, catalysts after calcination at 1073 K were used. Prior to TPR, the catalysts were pre-treated under flowing He and elevating temperature to 1073 K at 10 K/min. TPR was carried out under flowing 5% H_2 in Ar and elevating temperature from room temperature to 1073 K at 5 K/min.