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# Selective conversion of methane to ethane and hydrogen over In/molecular-sieve-3A catalyst†

Ayumi Nakaya,[a] Ayako Suzuki,[a] Shoji Iguchi [ab] and Ichiro Yamanaka *[a]

Direct conversion of methane to valuable chemicals has gained much attention. Besides, silica-supported liquid–metal indium catalysts (In/$SiO_2$) for the direct dehydrogenative conversion of methane (DCM) to higher hydrocarbons with 4% yield and 70% selectivity at 1173 K have been reported. In this work, In catalyst was found to be an excellent catalyst for the DCM reaction and selective formation of ethane and hydrogen without carbon deposition at the lower temperature of 873 K. The catalytic activity of In was strongly depended on supports at 873 K, and the molecular-sieve-3A (MS3A)-support calcined at 1123 K was more effective than the $SiO_2$ support. Selective conversion of methane to ethane and hydrogen proceeded on the In/MS3A catalyst. The role of the MS3A support in the DCM reaction is discussed.

## 1. Introduction

The conversion of $CH_4$ as a major component of natural gas into useful chemicals is one of the hot topics to curb the depletion of oil. Currently, $CH_4$ is used as a source of thermal energy and electric power. Except for methanol synthesis and the Fischer–Tropsch process, the catalytic technology for the direct conversion of $CH_4$ into useful chemicals does not exist. Therefore, studies on new catalysts and reactions are essential for developing the direct conversion process of $CH_4$.

Several chemists have been studying catalysts and reactions for the conversion of $CH_4$; however, strong C–H bonds and a symmetric molecular form of $CH_4$ are the major problems for the activation of $CH_4$.[1] Two scientific fields involving pioneering works are in existence, one is the oxidative coupling of $CH_4$ (OCM) to $C_2H_6$ and $C_2H_4$ with $O_2$ (ref. 2–4) and the other is a dehydrogenative conversion of $CH_4$ (DCM) or none-oxidative coupling of $CH_4$ (NOCM) to higher hydrocarbons.[5–8] In the latter field, most of the studies have focused on catalysis involving transition metal elements (Mo, Fe, Ni, *etc.*) because of their strong catalysis of the activation of C–H bonds. In our study, we focused on the post-transition metal elements (Ga, In, Bi, Sn) because of their mild catalysis of the activation of C–H bonds and found that the $SiO_2$-supported indium catalyst (In/$SiO_2$) showed higher catalytic activity for the DCM reaction.[7]

The In/$SiO_2$ catalyst showed a good result with 70% combined selectivity to hydrocarbons (ethylene, ethane, propylene, benzene, and toluene) with 4% conversion of $CH_4$ at 1173 K. The particular nature of the In/$SiO_2$ catalyst is that the metallic liquid of In shows catalysis for the activation of $CH_4$. This unique property of the In metal liquid for the DCM reaction has been studied by kinetic studies, isotope effects studies, first-principle DFT MD calculations,[9] and XAFS observations.[10] The major conclusions from our previous studies are as follows; (i) In metal liquid is thermally activated, (ii) the activated In species, In–In cluster models, can cleave a C–H bond of $CH_4$ to $CH_3$–In and H–In species, then, couplings of the two $CH_3$–In species produce $C_2H_6$ and of the two H–In species produce $H_2$, and (iii) the onset temperature of the activation of $CH_4$ by In liquid metal was observed approximately at 850 K using temperature programed reaction (TPR) studies and mass spectra analysis, but a quantitative analysis could not be performed.[11]

In this study, we found that the In catalyst showed significant catalytic activity in the DCM reaction at a lower temperature of 873 K and the support materials strongly affected the In catalysis; especially, molecular sieve 3A (MS3A) was effective. This work aimed to clarify the effects of the MS3A support on In catalysis approximately at 873 K and to propose functions of the MS3A support to enhance the catalytic activity of In in the DCM reaction.

## 2. Experimental

In/$SiO_2$ catalyst was prepared by a conventional impregnation method.[7,11] Several $SiO_2$ supports (CARiACT Q-3, CARiACT Q-30, Admafine SO-E6, AEROSIL 300) were calcined in air at 1173 K before the catalyst preparations (ESI†). The $SiO_2$ support was added to $In(NO_3)\cdot nH_2O$ solution, and this

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[a] *Department of Chemical Science and Engineering, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo, 152-8552, Japan. E-mail: yamanaka.i.aa@m.titech.ac.jp*
[b] *Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto, 615-8510, Japan*

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mixture was strongly stirred using a magnetic spin-bar. The suspension was dried at 353 K under stirring. The catalyst-precursor powder was calcined in air for 3 h at 773 K. After the calcined powder was reduced in a stream of $H_2$ at 1173 K for 3 h, In/$SiO_2$ catalysts were obtained. A loading of $In^0$ was 10 wt%.

The In/MS3A catalyst was prepared following a similar method to the In/$SiO_2$ catalyst. Different procedures were used for the calcination of MS3A (Wako Pure Chemical Industries) at 1023 K and reduction of $InO_x$/MS3A with $H_2$ at 1023 K. A loading of $In^0$ was the same as 10 wt%.

We prepared different types of In/MS3A catalysts as follows; the catalyst precursor of $InO_x$/MS3A was held in saturated water vapor at 45 °C. This humidified $InO_x$/MS3A material was reduced with pure $H_2$ at 1173 K under the same reduction procedure of In/$SiO_2$ and In/MS3A catalysts. The prepared catalyst was called In/MS3A(humid). In a similar way, In/MS4A(humid), In/LTA(humid), and In/$SiO_2$(humid) catalysts were prepared.

A fixed-bed quartz reactor (I.D. 12 mm) was used for the DCM reaction with 100 mg of the catalyst (Fig. S1†). After Ar was flown through the reactor to replace air, $H_2$ was flown at 20 mL $min^{-1}$ and the temperature was raised to 873 K at 25 K $min^{-1}$ and holding for 60 min. The reduction temperature was raised to 1023 K and lowered to the reaction temperature. After $H_2$ was replaced with Ar for 60 min, $CH_4$ was flown at 10 mL $min^{-1}$and the DCM reaction was initiated.[7,8,11]

Products were analyzed using a gas chromatograph (GC). $CH_4$, $C_2H_6$, and $C_2H_4$ were analyzed using a GC with a frame ionization detector (GC-8A-FID, Shimadzu) equipped with an Unibeads 1S column (3$\varphi$, 2 m). $H_2$ was analyzed using a GC with a thermal conductivity detector (GC-8A-TCD, Shimadzu) equipped with an activated carbon column (3$\varphi$, 2 m). Conversion of $CH_4$, selectivity to $C_2H_6$, and selectivity to $C_2H_4$ in the DCM reaction were calculated from eqn (1)–(3), respectively. These calculations were based on the hydrogen balance of the output gas mixture.[7,8,11]

$$\text{CH}_4\text{ conversion} = \frac{2\times \text{FR}(\text{H}_2)+6\times \text{FR}(\text{C}_2\text{H}_6)+4\times \text{FR}(\text{C}_2\text{H}_4)}{2\times \text{FR}(\text{H}_2)+6\times \text{FR}(\text{C}_2\text{H}_6)+4\times \text{FR}(\text{C}_2\text{H}_4)+4\times \text{DR}(\text{CH}_4)} \times 100(\%) \tag{1}$$

$$\text{C}_2\text{H}_6\text{ selectivity} = \frac{8\times \text{FR}(\text{C}_2\text{H}_6)}{2\times \text{FR}(\text{H}_2)+6\times \text{FR}(\text{C}_2\text{H}_6)+4\times \text{FR}(\text{C}_2\text{H}_4)} \times 100(\%) \tag{2}$$

$$\text{C}_2\text{H}_4\text{ selectivity} = \frac{8\times \text{FR}(\text{C}_2\text{H}_4)}{2\times \text{FR}(\text{H}_2)+6\times \text{FR}(\text{C}_2\text{H}_6)+4\times \text{FR}(\text{C}_2\text{H}_4)} \times 100(\%) \tag{3}$$

(FR($H_2$, $C_2H_6$, $C_2H_4$): formation rate of $H_2$, $C_2H_6$, $C_2H_4$ (mol $min^{-1}$), DR($CH_4$): detection rate of $CH_4$ (mol $min^{-1}$)).

Brief characterization studies for the catalysts were conducted by XRD analysis (MiniFlex-600/TISS, Rigaku Co.) and gas-adsorption measurement (BELSORP-mini II, MicrotracBEL Co.).

## 3. Results and discussion

### 3.1 Catalysis of In(*I*) at a lower temperature

As mentioned in the introduction section, the previous results of the temperature-programed-reaction study for $CH_4$ conversion on the In/$SiO_2$ catalyst obtained using a mass spectrometer suggested that the activation of C–H bonds of $CH_4$ would proceed at a lower temperature approximately at 850 K than at 1173 K, which was a typical condition for the DCM reaction producing higher hydrocarbons.[7,11] Therefore, the DCM reaction was studied under steady reaction conditions at 873 K to clarify the formation of products at 873 K by the GC analysis.

Fig. 1 shows the time course for the formation of $C_2H_6$ and $H_2$ over the In/$SiO_2$ catalyst at 873 K. At a blank test, without the In/$SiO_2$ catalyst, no formation of $C_2H_6$ and $H_2$ was not observed at 873 K. The formation rate of $C_2H_6$ gradually decreased with process time until 120 min and the steady formation was observed after 150 min. The formation rate of $H_2$ gradually decreased similar to that of $C_2H_6$. The formation rate of $C_2H_6$ was lower than that of $H_2$ for 120 min. In contrast, both formation rates were almost equal from 150 min to 240 min. The change in the formation rates impacted the selectivity to $C_2H_6$ as shown in Fig. 1. In the first half, until 120 min, an apparent selectivity to $C_2H_6$ was about 95% and the selectivity was almost 100% in the second half after 180 min. The stoichiometric conversion of $CH_4$ to $C_2H_6$ and $H_2$ continuously proceeded after 180 min (eqn (4)). The selectivity below 100% means that there were unidentified hydrocarbons, or carbon deposition forms (eqn (5)). The average results during 180 min are indicated in run 1 of Table 1.

$$2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2 \quad \Delta H^0 = +66\ \text{kJ mol}^{-1} \tag{4}$$

$$\text{CH}_4 \rightarrow \text{C}_{(s)} + 2\text{H}_2 \quad \Delta H^0 = +75\ \text{kJ mol}^{-1} \tag{5}$$

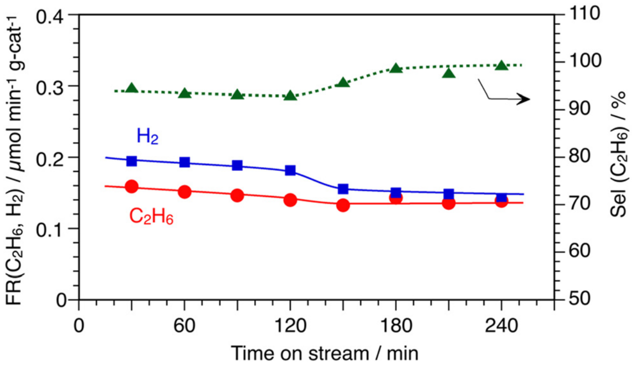

**Fig. 1** Time courses of DCM reaction by In/$SiO_2$ catalyst at 873 K. $CH_4$: 1 atm and 10 mL $min^{-1}$, catalyst: 10 wt% In/$SiO_2$.

**Table 1** Results of the DCM reaction by various catalysts of In compounds at 873 K

| | | Form. rate ($\mu$mol min$^{-1}$ $g_{cat}$$^{-1}$) | | Select. (%) |
|---|---|---|---|---|
| Run | Catalyst | $C_2H_6$ | $H_2$ | $C_2H_6$ |
| 1 | $In/SiO_2$ | 0.15 | 0.18 | 96 |
| 2 | $In_2O_3/SiO_2$ | 0.05 | 1.82 | 10 |
| 3 | $In/Al_2O_3$ | 0.03 | 1.80 | 6 |
| 4 | $In/TiO_2$ | 0.16 | 0.87 | 47 |
| 5 | $In/Nb_2O_5$ | 0.05 | 0.47 | 32 |
| 6 | $In/ZrO_2$ | 0.08 | 3.08 | 10 |
| 7 | $In/CeO_2$ | 0.23 | 2.41 | 30 |
| 8 | In/MgO | 0.19 | 25.4 | 3 |

$CH_4$: 1 atm and 10 mL min$^{-1}$, catalysts: 10 wt% In loading and 100 mg in the reactor.

When $In_2O_3/SiO_2$ material, as a precursor of the $In/SiO_2$ catalyst before the reduction, was used in the DCM reaction, a lower formation rate of $C_2H_6$ and a higher formation rate of $H_2$ were observed at run 2, as shown in Table 1. This clearly indicated that $In^0(l)$ was the active phase for the selective $C_2H_6$ formation at a lower temperature of 873 K and $SiO_2$ (CARiACT Q-3) is a good support for $In^0(l)$ catalyst.[10] To increase the catalytic activity of $In^0(l)$ catalyst, other oxide supports were tested for the DCM reaction, runs 3–8 in Table 1. All the oxide supports were calcined in air at 1173 K before the preparation of In/oxide support catalysts. The formation rates of $C_2H_6$ and $H_2$ were strongly affected by oxide supports. In the case of $CeO_2$ and MgO supports, the formation rates of $C_2H_6$ were enhanced but that of $H_2$ was strongly accelerated. On other supports, such as $Al_2O_3$, $TiO_2$, $Nb_2O_5$, and $ZrO_2$, the formation rates of $C_2H_6$ were suppressed and the decomposition rates were accelerated. Excess formation of $H_2$ was due to the decomposition of $CH_4$ to carbon deposits and $H_2$ formation. Except for the $SiO_2$ support, oxide supports were not suitable to achieve the selective conversion of $CH_4$ to $C_2H_6$ and $H_2$ by the $In^0(l)$ catalyst.

$In^0/SiO_2$ (CARiACT Q-3) catalyst showed excellent catalysis for the DCM reaction with over 96% selectivity to $C_2H_6$ and $H_2$ at 873 K. In order to clarify the nature of $SiO_2$ support for the DCM reaction, three $SiO_2$ materials, CARiACT Q-30, Admafine SO-E6, and AEROSIL 300, were tested as the support. All $SiO_2$ materials were calcined in air at 1173 K before $In(NO_3)_3$ impregnation, as mentioned in the experimental section. Fig. 2 shows the relationship between the formation rates of $C_2H_6$ and specific surface areas of $SiO_2$ supports calcined at 1173 K. As you can see clearly in Fig. 2, a $SiO_2$ support having a lower surface area was suitable for the selective formation of $C_2H_6$ by $In^0(l)$ catalyst. In contrast, decomposition of $CH_4$ to $H_2$ and carbon deposition proceeded on a $SiO_2$ support having a higher surface area. Of course, we confirmed that no decomposition of $CH_4$ occurred on the $SiO_2$ materials without the $In^0(l)$ catalyst at 873 K.

We have already reported the conversion mechanism of $CH_4$ to $C_2H_6$ and higher hydrocarbons catalyzed by the $In/SiO_2$ catalysts at a higher temperature of 1173 K, as mentioned in the introduction.[9,11] The brief reaction mechanism is as follows; (i) In liquid metal catalyzes the activation of the C–H bond of $CH_4$, (ii) $CH_3$–In($l$) and H–In($l$) species are produced, then, (iii) two $CH_3$–In($l$) species on the liquid surface were coupled and produced $C_2H_6$, (iv) H species on In diffused into a bulk phase of In($l$), (v) two H species were dissolved in the bulk In($l$) were coupled at the surface and desorbed as $H_2$.

When a $SiO_2$ support with a lower surface area was used, the same reaction mechanism could be applied on the $In^0(l)$ catalyst at 873 K, and $C_2H_6$ and $H_2$ were selectively produced. Whereas, we propose a side reaction path over the $SiO_2$ support with higher surface area in that $CH_3$ species on In($l$) migrate to the surface of the $SiO_2$ support before the coupling reaction and decompose to carbon and hydrogen by surface catalysis of $SiO_2$. If this mechanism was true then an inert surface of supports should be suitable to promote selective coupling of $CH_3$ species on the surface of In($l$).

### 3.2 Acceleration of In($l$) catalysis by molecular sieve 3A

As mentioned above, the $In^0/SiO_2$ (CARiACT Q-3) catalyst showed high selectivity to the conversion of $CH_4$ to $C_2H_6$ and $H_2$; however, the conversion of $CH_4$, as shown in Fig. 1 was only 0.004%, which was calculated from the product yields by GC (eqn (1)). The thermodynamic equilibrium conversion of this reaction was about 0.9% at 873 K. We have considered that the formation rate of $C_2H_6$ through the coupling of $CH_3$ species was suppressed by the equilibrium between $CH_3$ species and H species on the surface of $In^0(l)$.[11] In other words, if we could accelerate the elimination of H species from the surface of $In^0(l)$, the recombination reaction between $CH_3$ and H species decelerated and the coupling reaction of $CH_3$ species accelerated.

How to accelerate the elimination of H species on $In^0(l)$ is an essential topic and we came up with an idea for the

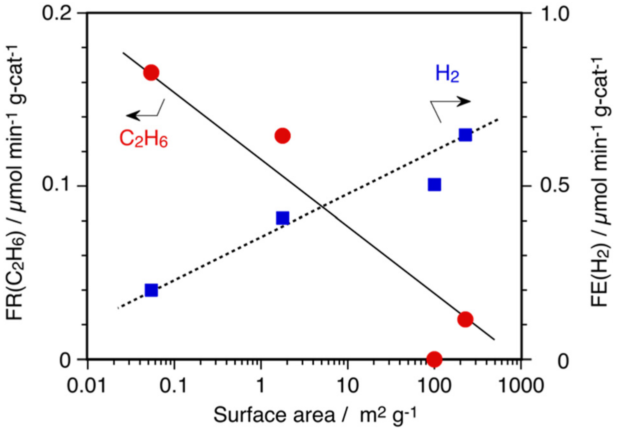

**Fig. 2** Influence of surface area of $SiO_2$ support on DCM reaction by 10 wt% $In/SiO_2$ catalysts at 873 K. Amount of catalyst: 100 mg, $CH_4$: 1 atm and 10 mL min$^{-1}$.

**Table 2** Results of the DCM reaction by In/molecular-sieve catalysts at 873 K

| | | Format. rate (μmol $min^{-1}$ $g_{cat}{}^{-1}$) | | | Select. (%) |
|---|---|---|---|---|---|
| Run | Catalyst | $C_2H_6$ | $C_2H_4$ | $H_2$ | $C_2H_6$ + $C_2H_4$ |
| 1 | 10 wt% In/$SiO_2$ | 0.15 | 0.00 | 0.18 | 96 |
| 9 | 10 wt% In/MS3A | 0.89 | 0.05 | 0.52 | 98 |
| 10 | 10 wt% In/MS3A(humid) | 1.25 | 0.08 | 1.16 | 104 |
| 11 | 10 wt% In/$SiO_2$(humid) | 0.28 | 0.01 | 0.42 | 90 |
| 12 | 10 wt% In/MS4A(humid) | 0.30 | 0.01 | 0.65 | 79 |
| 13 | 10 wt% In/H-LTA(humid) | 0.41 | 0.02 | 0.95 | 78 |
| 14 | 5 wt% In/MS3A(humid) | 0.15 | 0.00 | 1.07 | 41 |
| 15 | 20 wt% In/MS3A(humid) | 1.74 | 0.12 | 1.27 | 109 |
| 16 | 30 wt% In/MS3A(humid) | 0.96 | 0.05 | 0.95 | 102 |

$CH_4$: 1 atm and 10 mL $min^{-1}$, catalysts: 100 mg in the reactor.

acceleration. Our idea is the utilization of the function of the molecular sieve for the elimination of H species, that is to separate $CH_3$ and H species using a molecular sieve. A molecular sieve-3A (MS3A) has micropores of about 0.3 nm in which H species can be introduced but not the $CH_4$ and $CH_3$ species. If this hypothesis is true, H species on and in $In^0(l)$ will spill over and diffuse into the MS3A and coupling reaction of the $CH_3$ species to accelerate the formation of $C_2H_6$.

In/MS3A catalyst was prepared by the impregnation method similar to that of the In/$SiO_2$ catalyst. The MS3A support was calcined in air at 1023 K before the preparation of the catalyst, as described in the Experimental section. The catalytic activity of In/MS3A at 873 K is indicated in run 9 shown in Table 2. Comparing runs 1 and 9, the formation rate of $C_2H_6$ on the In/MS3A catalyst was significantly accelerated, and it was 5 times higher than that on the In/$SiO_2$ catalyst. In addition, $C_2H_4$ formed on the In/MS3A catalyst at 873 K though the selectivity was only 2%. The total selectivity of $C_2H_6$ and $C_2H_4$ was 98% and a stoichiometric conversion of $CH_4$ to $C_2H_6$, $C_2H_4$, and $H_2$ was performed.

To improve the catalytic activity of the In/MS3A catalyst, we studied influences of the preparation conditions of the catalyst, calcination temperature and time, reduction temperature and time, partial pressure of $H_2$ and reduction temperature, *etc.* We have found that humidity around the catalyst precursor, $InO_x$/MS3A, influenced the catalytic activity of the In/MS3A catalyst and this was named In/MS3A(humid). Preparation procedures are mentioned in the Experimental section. It was observed that for run 10, the formation rate of $C_2H_6$ was accelerated 1.4 times by the humidifying treatment and the total selectivity of $C_2H_6$ and $C_2H_4$ was 104%, as calculated from eqn (2). The selectivity of over 100% indicated less formation of $H_2$ in comparison to the hydrocarbon formation. As a reference, the In/$SiO_2$(humid) catalyst was applied in the DCM reaction. As indicated, at run 11, a little acceleration of $C_2H_6$ formation was observed by the humidification treatment of $InO_x$/$SiO_2$.

To reveal the unique function of the MS3A support, MS4A and LTA materials were also applied for the supports.[12,13] In/MS4A(humid) and In/LTA(humid) catalysts were prepared using the above procedures and the results are shown as runs 12 and 13 in Table 2, respectively. Accelerations for the $C_2H_6$ formation rate by MS4A and LTA supports were clear from the data of the runs 10–13. In addition, the selectivity to $C_2H_6$ decreased using MS4A and LTA supports, and carbon deposition should proceed.

Effects of In loadings from 5 to 30 wt% over the MS3A support on the DCM reaction were studied, as shown in runs 10, 14–16. The 5 wt% In/MS3A(humid) catalyst showed a lower formation rate of $C_2H_6$ and a good rate for $H_2$, corresponding to a lower selectivity to $C_2H_6$. 20 wt% In/MS3A(humid) catalyst showed the highest catalytic activity and the highest total selectivity for $C_2H_6$ and $C_2H_4$ over 100%.

Time courses for the total formation of $C_2H_6$ and $C_2H_4$ on the In/MS3A(humid), In/MS4A(humid), and In/$SiO_2$(humid) catalysts are shown in Fig. 3. The formation rate of $C_2H_6$ and $C_2H_4$ over the In/MS3A(humid) catalyst was far higher than that of the In/$SiO_2$(humid) catalyst at

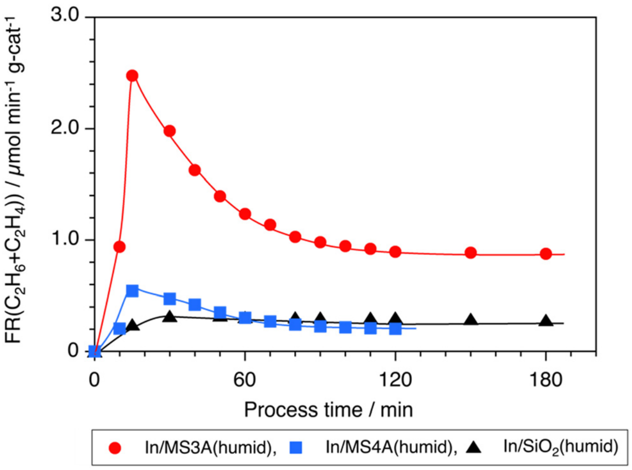

**Fig. 3** Time courses of the formation rate of the sum of $C_2H_6$ and $C_2H_4$ by 10 wt% In/MS3A(humid), 10 wt% In/MS4A(humid), and 10 wt% In/$SiO_2$(humid) catalysts. Amount of catalyst 100 mg, $CH_4$: 1 atm and 10 mL $min^{-1}$.

the initial stage of the reaction and decreased with the process time. However, significant acceleration of the $C_2H_6$ formation on the In/MS3A(humid) catalyst was observed at 180 min. The selectivity to $C_2H_4$ was constant during the reaction; 7% on In/MS3A(humid), and 3% on In/MS4A(humid) and In/$SiO_2$(humid) catalysts.

Fig. 4 shows the effects of the reaction temperatures on (a) the formation rate of the total $C_2H_6$ and $C_2H_4$ and (b) their selectivity on In/MS3A(humid), In/MS4A(humid), and In/$SiO_2$(humid) catalysts. The In/MS3A(humid) catalyst showed significant catalytic activity and a higher selectivity of 90% to $C_2H_6$ at a lower temperature of 773 K, at which the In/MS4A(humid) and In/$SiO_2$(humid) catalysts did not work. In addition, the In/MS3A(humid) catalyst showed catalytic activity even at 723 K through a lower selectivity. An advantage of In/MS3A(humid) catalyst against In/MS4A(humid) and In/$SiO_2$(humid) catalysts for the activation and conversion of $CH_4$ was clear. Apparent activation energies over In/MS3A(humid), In/MS4A(humid), and In/$SiO_2$(humid) catalysts were calculated from the Arrhenius plots and were 16.2, 15.4, and 20.6 kJ $mol^{-1}$, respectively (Fig. S2†). These apparent activation energies were too low to compare the cleavage energy of 463 kJ $mol^{-1}$ in the C–H bond of $CH_4$. When the rate-determining step was the C–H bond activation in the DCM reaction, higher activation energies of 170 kJ $mol^{-1}$ for the In/$SiO_2$ catalyst[11] and 250 kJ $mol^{-1}$ for the $Ni_2P$/$SiO_2$ catalyst[8] were reported at higher reaction temperatures over 1000 K. In other words, the diffusion process should affect the apparent lower activation energies over the In/MS3A(humid), In/MS4A(humid), and In/$SiO_2$(humid) catalysts below 873 K.

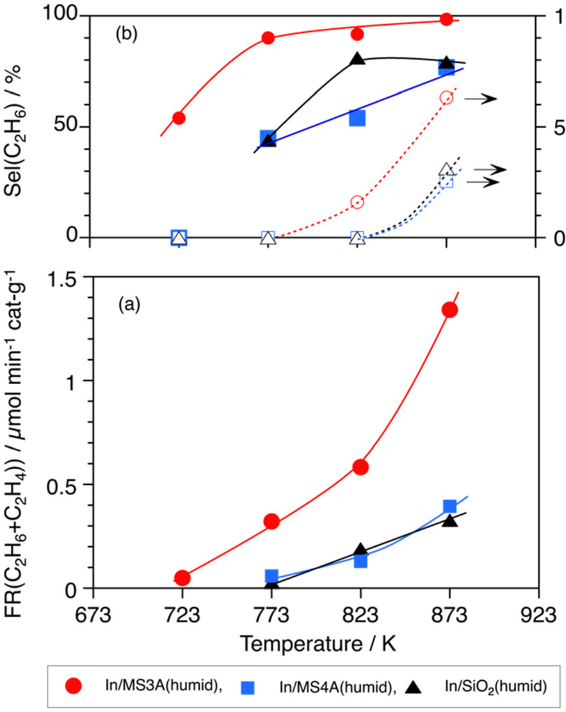

**Fig. 4** Effects of reaction temperatures on the DCM reaction by 10 wt% In/MS3A(humid), 10 wt% In/MS4A(humid), and 10 wt% In/$SiO_2$(humid) catalysts. (a) Formation rate of the sum of $C_2H_6$ and $C_2H_4$; and (b) selectivity to $C_2H_6$ and $C_2H_4$. Amount of catalyst: 100 mg, $CH_4$: 1 atm and 10 mL $min^{-1}$.

As mentioned above, the In/MS3A(humid) catalyst showed significant catalytic activity for the DCM reaction, a high formation rate, and a high selectivity of over 100%. The selectivity higher than 100% means a lower formation rate of $H_2$ compared with the total formation of $C_2H_6$ and $C_2H_4$. The selectivity lower than 100% means carbon deposition or undetected product formation. In the former case, the lower formation of $H_2$ is very strange because the stable form of hydrogen is only $H_2$. If counter materials (molecules) were coupled with hydrogen species, $H^\bullet$, $H^+$, and $H^-$ species were stabilized. For example, $H^\bullet$ (metal surface), $H^+$ (anion species), and $H^-$ (cation species) forms are stable. We can accurately quantify $H_2$ by the GC analysis, but $H^\bullet$, $H^+$, and $H^-$ species on the support cannot be quantified. In the latter case, the apparent selectivity to the $C_2H_6$ and $C_2H_4$ total was over 100% because hydrogen species were held on the catalyst.

## 4. Discussion

Basic characterization studies for In/MS3A(humid), In/MS4A(humid), and In/$SiO_2$(humid) catalysts were conducted using XRD and $N_2$ adsorption measurements. Fig. 5 shows the XRD patterns of the three catalysts. Diffraction patterns of $In^0$ were clearly observed for the three catalysts. Original diffraction patterns indicated that MS-3A and MS-4A were not observed for the In/MS3A(humid) and In/MS4A(humid) catalysts. Diffraction patterns of MS3A and MS4A calcined at 1123 K were measured and particular diffraction patterns of MS3A and MS4A disappeared. Outer surface areas of MS3A and MS4A measured by BET method using $N_2$ decreased from 18.5 to 0.4 $m^2$ $g^{-1}$ and from 9.8 to 1.2 $m^2$ $g^{-1}$, respectively, by

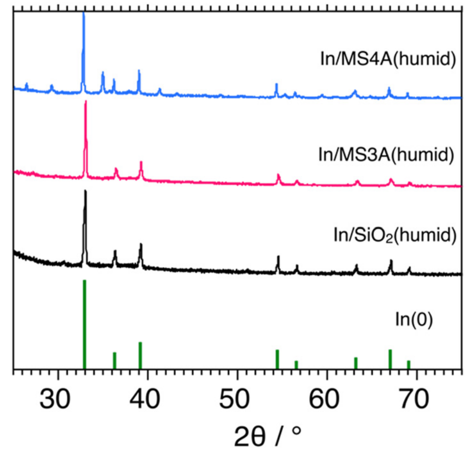

**Fig. 5** XRD patterns of 10 wt% In/MS3A(humid), 10 wt% In/MS4A(humid), and 10 wt% In/$SiO_2$(humid) flesh catalysts.

calcination at 1023 K. These observations suggest that the original crystal structures of MS3A and MS4A were decomposed by calcination; however, a part of the original pores of MS3A and MS4A would remain after the calcination. Therefore, we can observe differences in the catalytic activities between the In/MS3A(humid), In/MS4A(humid), and In/$SiO_2$(humid) catalysts for the DCM reaction.

Effective pore diameters of the original MS3A, MS4A, and LTA materials were 0.3, 0.4, and 0.5 nm, respectively. As mentioned above, we raised the idea of separating $CH_3$ and H species by the function of a molecular sieve. The micropores of MS3A were 0.3 nm in size, in which H species (<0.3 nm) can be introduced but $CH_4$ (3.8 nm) and maybe $CH_3$ species cannot be introduced. If this model is true, the recombination of $CH_3$ species and H species is suppressed, and the coupling of two $CH_3$ species is accelerated producing $C_2H_6$. On the other hand, both H and $CH_3$ species can diffuse into a wide pore of MS4A and the recombination between H and $CH_3$ species proceeds reproducing $CH_4$. This situation is similar to that of the $SiO_2$ support. Therefore, catalytic activities on the In/MS4(humid) and In/$SiO_2$(humid) catalysts were very similar, as shown in Fig. 3 and Table 2. We consider that the separation of H and $CH_3$ species on the In(*l*) surface by the micropores of MS3A (0.3 nm) is essential for $C_2H_6$ formation, as described above. We speculate that H species accumulate in the micropores and acceleration of H species removal in the micropores is essential to enhance the formation rate of $C_2H_6$. We have a plan to prove the accumulation of hydrogen species in micropores of the In/MS3A(humid) catalyst by applying TPD experiments in future work.

## Conflicts of interest

There are no conflicts to declare.

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