

Cite this: *Catal. Sci. Technol.*, 2023,
13, 6712Received 2nd September 2023,
Accepted 16th October 2023

DOI: 10.1039/d3cy01217d

rsc.li/catalysis

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/SiO₂) 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 SiO₂ 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 CH₄ as a major component of natural gas into useful chemicals is one of the hot topics to curb the depletion of oil. Currently, CH₄ 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 CH₄ into useful chemicals does not exist. Therefore, studies on new catalysts and reactions are essential for developing the direct conversion process of CH₄.

Several chemists have been studying catalysts and reactions for the conversion of CH₄; however, strong C–H bonds and a symmetric molecular form of CH₄ are the major problems for the activation of CH₄.¹ Two scientific fields involving pioneering works are in existence, one is the oxidative coupling of CH₄ (OCM) to C₂H₆ and C₂H₄ with O₂ (ref. 2–4) and the other is a dehydrogenative conversion of CH₄ (DCM) or none-oxidative coupling of CH₄ (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 SiO₂-supported indium catalyst (In/SiO₂) showed higher catalytic activity for the DCM reaction.⁷

The In/SiO₂ catalyst showed a good result with 70% combined selectivity to hydrocarbons (ethylene, ethane, propylene, benzene, and toluene) with 4% conversion of CH₄ at 1173 K. The particular nature of the In/SiO₂ catalyst is that the metallic liquid of In shows catalysis for the activation of CH₄. 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 CH₄ to CH₃–In and H–In species, then, couplings of the two CH₃–In species produce C₂H₆ and of the two H–In species produce H₂, and (iii) the onset temperature of the activation of CH₄ by In liquid metal was observed approximately at 850 K using temperature programmed 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/SiO₂ catalyst was prepared by a conventional impregnation method.^{7,11} Several SiO₂ supports (CARIACT Q-3, CARIACT Q-30, Admagine SO-E6, AEROSIL 300) were calcined in air at 1173 K before the catalyst preparations (ESI†). The SiO₂ support was added to In(NO₃)₃·*n*H₂O solution, and this

^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

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3cy01217d>

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 H₂ at 1173 K for 3 h, In/SiO₂ catalysts were obtained. A loading of In⁰ was 10 wt%.

The In/MS3A catalyst was prepared following a similar method to the In/SiO₂ catalyst. Different procedures were used for the calcination of MS3A (Wako Pure Chemical Industries) at 1023 K and reduction of InO_x/MS3A with H₂ at 1023 K. A loading of In⁰ 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 H₂ at 1173 K under the same reduction procedure of In/SiO₂ and In/MS3A catalysts. The prepared catalyst was called In/MS3A(humid). In a similar way, In/MS4A(humid), In/LTA(humid), and In/SiO₂(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, H₂ 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 H₂ was replaced with Ar for 60 min, CH₄ was flown at 10 mL min⁻¹ and the DCM reaction was initiated.^{7,8,11}

Products were analyzed using a gas chromatograph (GC). CH₄, C₂H₆, and C₂H₄ were analyzed using a GC with a flame ionization detector (GC-8A-FID, Shimadzu) equipped with an Unibeads 1S column (3φ, 2 m). H₂ was analyzed using a GC with a thermal conductivity detector (GC-8A-TCD, Shimadzu) equipped with an activated carbon column (3φ, 2 m). Conversion of CH₄, selectivity to C₂H₆, and selectivity to C₂H₄ 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}

CH₄ conversion

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

C₂H₆ selectivity

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

C₂H₄ selectivity

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

(FR(H₂, C₂H₆, C₂H₄): formation rate of H₂, C₂H₆, C₂H₄ (mol min⁻¹), DR(CH₄): detection rate of CH₄ (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-programmed-reaction study for CH₄ conversion on the In/SiO₂ catalyst obtained using a mass spectrometer suggested that the activation of C–H bonds of CH₄ 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 C₂H₆ and H₂ over the In/SiO₂ catalyst at 873 K. At a blank test, without the In/SiO₂ catalyst, no formation of C₂H₆ and H₂ was not observed at 873 K. The formation rate of C₂H₆ gradually decreased with process time until 120 min and the steady formation was observed after 150 min. The formation rate of H₂ gradually decreased similar to that of C₂H₆. The formation rate of C₂H₆ was lower than that of H₂ 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 C₂H₆ as shown in Fig. 1. In the first half, until 120 min, an apparent selectivity to C₂H₆ was about 95% and the selectivity was almost 100% in the second half after 180 min. The stoichiometric conversion of CH₄ to C₂H₆ and H₂ 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.

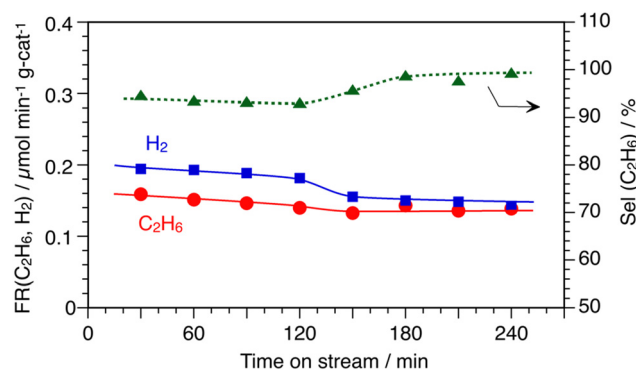
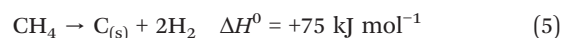
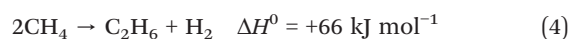


Fig. 1 Time courses of DCM reaction by In/SiO₂ catalyst at 873 K. CH₄: 1 atm and 10 mL min⁻¹, catalyst: 10 wt% In/SiO₂.

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

Run	Catalyst	Form. rate ($\mu\text{mol min}^{-1} \text{g}_{\text{cat}}^{-1}$)		Select. (%)
		C_2H_6	H_2	C_2H_6
1	In/SiO ₂	0.15	0.18	96
2	In ₂ O ₃ /SiO ₂	0.05	1.82	10
3	In/Al ₂ O ₃	0.03	1.80	6
4	In/TiO ₂	0.16	0.87	47
5	In/Nb ₂ O 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

CH₄: 1 atm and 10 mL min⁻¹, catalysts: 10 wt% In loading and 100 mg in the reactor.

When In₂O₃/SiO₂ material, as a precursor of the In/SiO₂ catalyst before the reduction, was used in the DCM reaction, a lower formation rate of C₂H₆ and a higher formation rate of H₂ were observed at run 2, as shown in Table 1. This clearly indicated that In⁰(*l*) was the active phase for the selective C₂H₆ formation at a lower temperature of 873 K and SiO₂ (CARIAct Q-3) is a good support for In⁰(*l*) catalyst.¹⁰ To increase the catalytic activity of In⁰(*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 C₂H₆ and H₂ were strongly affected by oxide supports. In the case of CeO₂ and MgO supports, the formation rates of C₂H₆ were enhanced but that of H₂ was strongly accelerated. On other supports, such as Al₂O₃, TiO₂, Nb₂O₅, and ZrO₂, the formation rates of C₂H₆ were suppressed and the decomposition rates were accelerated. Excess formation of H₂ was due to the decomposition of CH₄ to carbon deposits and H₂ formation. Except for the SiO₂ support, oxide supports were not suitable to achieve the selective conversion of CH₄ to C₂H₆ and H₂ by the In⁰(*l*) catalyst.

In⁰/SiO₂ (CARIAct Q-3) catalyst showed excellent catalysis for the DCM reaction with over 96% selectivity to C₂H₆ and H₂ at 873 K. In order to clarify the nature of SiO₂ support for the DCM reaction, three SiO₂ materials, CARIAct Q-30, Admafine SO-E6, and AEROSIL 300, were tested as the support. All SiO₂ materials were calcined in air at 1173 K before In(NO₃)₃ impregnation, as mentioned in the experimental section. Fig. 2 shows the relationship between the formation rates of C₂H₆ and specific surface areas of SiO₂ supports calcined at 1173 K. As you can see clearly in Fig. 2, a SiO₂ support having a lower surface area was suitable for the selective formation of C₂H₆ by In⁰(*l*) catalyst. In contrast, decomposition of CH₄ to H₂ and carbon deposition proceeded on a SiO₂ support having a higher surface area. Of course, we confirmed that no decomposition of CH₄ occurred on the SiO₂ materials without the In⁰(*l*) catalyst at 873 K.

We have already reported the conversion mechanism of CH₄ to C₂H₆ and higher hydrocarbons catalyzed by the In/

SiO₂ 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 CH₄, (ii) CH₃–In(*l*) and H–In(*l*) species are produced, then, (iii) two CH₃–In(*l*) species on the liquid surface were coupled and produced C₂H₆, (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 H₂.

When a SiO₂ support with a lower surface area was used, the same reaction mechanism could be applied on the In⁰(*l*) catalyst at 873 K, and C₂H₆ and H₂ were selectively produced. Whereas, we propose a side reaction path over the SiO₂ support with higher surface area in that CH₃ species on In(*l*) migrate to the surface of the SiO₂ support before the coupling reaction and decompose to carbon and hydrogen by surface catalysis of SiO₂. If this mechanism was true then an inert surface of supports should be suitable to promote selective coupling of CH₃ species on the surface of In(*l*).

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

As mentioned above, the In⁰/SiO₂ (CARIAct Q-3) catalyst showed high selectivity to the conversion of CH₄ to C₂H₆ and H₂; however, the conversion of CH₄, 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 C₂H₆ through the coupling of CH₃ species was suppressed by the equilibrium between CH₃ species and H species on the surface of In⁰(*l*).¹¹ In other words, if we could accelerate the elimination of H species from the surface of In⁰(*l*), the recombination reaction between CH₃ and H species decelerated and the coupling reaction of CH₃ species accelerated.

How to accelerate the elimination of H species on In⁰(*l*) is an essential topic and we came up with an idea for the

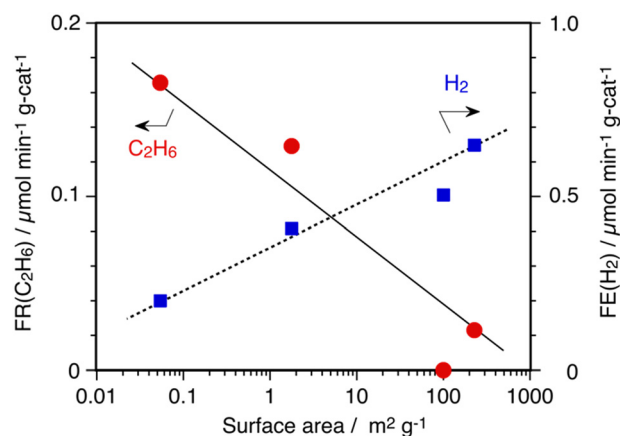


Fig. 2 Influence of surface area of SiO₂ support on DCM reaction by 10 wt% In/SiO₂ catalysts at 873 K. Amount of catalyst: 100 mg, CH₄: 1 atm and 10 mL min⁻¹.

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

Run	Catalyst	Format. rate ($\mu\text{mol min}^{-1} \text{g}_{\text{cat}}^{-1}$)			Select. (%) $\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$
		C_2H_6	C_2H_4	H_2	
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

CH₄: 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 CH₃ 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 CH₄ and CH₃ species. If this hypothesis is true, H species on and in In⁰(*l*) will spill over and diffuse into the MS3A and coupling reaction of the CH₃ species to accelerate the formation of C₂H₆.

In/MS3A catalyst was prepared by the impregnation method similar to that of the In/SiO₂ 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 C₂H₆ on the In/MS3A catalyst was significantly accelerated, and it was 5 times higher than that on the In/SiO₂ catalyst. In addition, C₂H₄ formed on the In/MS3A catalyst at 873 K though the selectivity was only 2%. The total selectivity of C₂H₆ and C₂H₄ was 98% and a stoichiometric conversion of CH₄ to C₂H₆, C₂H₄, and H₂ 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 H₂ 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 C₂H₆ was accelerated 1.4 times by the humidifying treatment and the total selectivity of C₂H₆ and C₂H₄ was 104%, as calculated from eqn (2). The selectivity of over 100% indicated less formation of H₂ in comparison to the hydrocarbon formation. As a reference, the In/SiO₂(humid) catalyst was applied in the DCM reaction. As indicated, at run 11, a little acceleration of C₂H₆ formation was observed by the humidification treatment of InO_x/SiO₂.

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 C₂H₆ formation rate by MS4A and LTA supports were clear from the data of the runs 10–13. In addition, the selectivity to C₂H₆ 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 C₂H₆ and a good rate for H₂, corresponding to a lower selectivity to C₂H₆. 20 wt% In/MS3A(humid) catalyst showed the highest catalytic activity and the highest total selectivity for C₂H₆ and C₂H₄ over 100%.

Time courses for the total formation of C₂H₆ and C₂H₄ on the In/MS3A(humid), In/MS4A(humid), and In/SiO₂(humid) catalysts are shown in Fig. 3. The formation rate of C₂H₆ and C₂H₄ over the In/MS3A(humid) catalyst was far higher than that of the In/SiO₂(humid) catalyst at

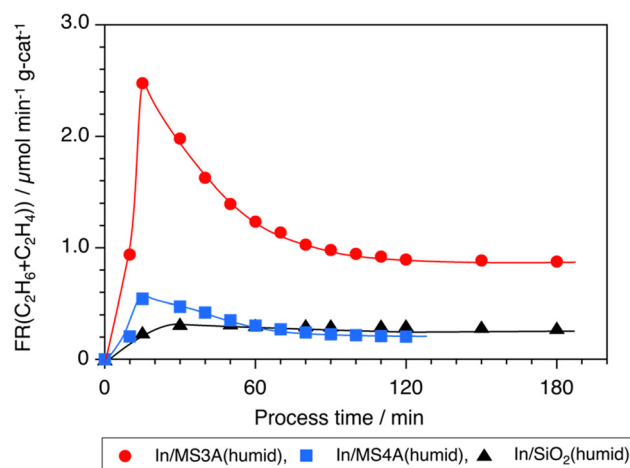


Fig. 3 Time courses of the formation rate of the sum of C₂H₆ and C₂H₄ by 10 wt% In/MS3A(humid), 10 wt% In/MS4A(humid), and 10 wt% In/SiO₂(humid) catalysts. Amount of catalyst 100 mg, CH₄: 1 atm and 10 mL min⁻¹.

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/SiO₂(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/SiO₂(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/SiO₂(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/SiO₂(humid) catalysts for the activation and conversion of CH_4 was clear. Apparent activation energies over In/MS3A(humid), In/MS4A(humid), and In/SiO₂(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/SiO₂ catalyst¹¹ and 250 kJ mol⁻¹ for the Ni₂P/

SiO₂ catalyst⁸ 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/SiO₂(humid) catalysts below 873 K.

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^{\cdot} , H^+ , and H^- species were stabilized. For example, H^{\cdot} (metal surface), H^+ (anion species), and H^- (cation species) forms are stable. We can accurately quantify H_2 by the GC analysis, but H^{\cdot} , 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/SiO₂(humid) catalysts were conducted using XRD and N₂ adsorption measurements. Fig. 5 shows the XRD patterns of the three catalysts. Diffraction patterns of In⁰ 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 N₂ decreased from 18.5 to 0.4 m² g⁻¹ and from 9.8 to 1.2 m² g⁻¹, respectively, by

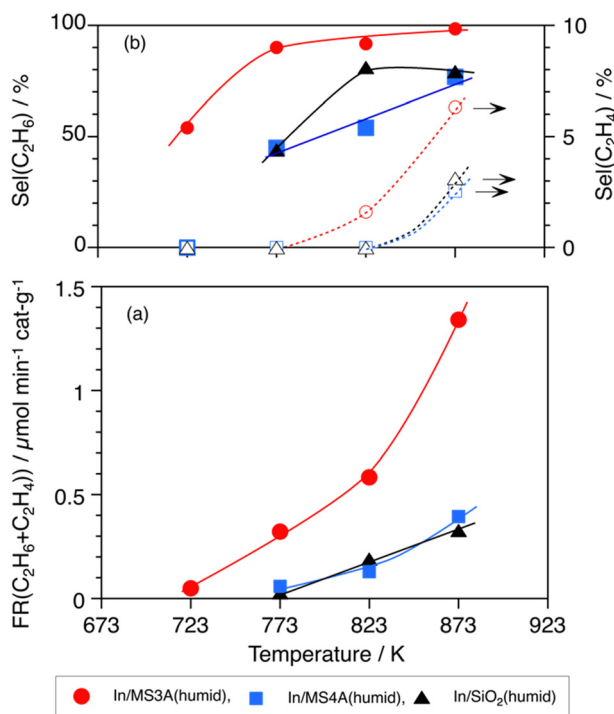


Fig. 4 Effects of reaction temperatures on the DCM reaction by 10 wt% In/MS3A(humid), 10 wt% In/MS4A(humid), and 10 wt% In/SiO₂(humid) catalysts. (a) Formation rate of the sum of C_2H_6 and C_2H_4 ; and (b) selectivity to C_2H_6 and C_2H_4 . Amount of catalyst: 100 mg, CH_4 : 1 atm and 10 mL min⁻¹.

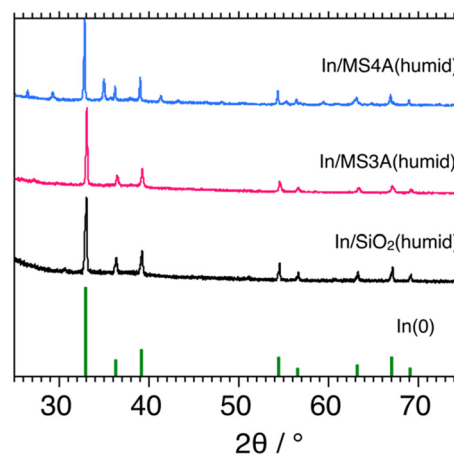


Fig. 5 XRD patterns of 10 wt% In/MS3A(humid), 10 wt% In/MS4A(humid), and 10 wt% In/SiO₂(humid) flesh catalysts.

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/SiO₂(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 CH₃ 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 CH₄ (3.8 nm) and maybe CH₃ species cannot be introduced. If this model is true, the recombination of CH₃ species and H species is suppressed, and the coupling of two CH₃ species is accelerated producing C₂H₆. On the other hand, both H and CH₃ species can diffuse into a wide pore of MS4A and the recombination between H and CH₃ species proceeds reproducing CH₄. This situation is similar to that of the SiO₂ support. Therefore, catalytic activities on the In/MS4(humid) and In/SiO₂(humid) catalysts were very similar, as shown in Fig. 3 and Table 2. We consider that the separation of H and CH₃ species on the In(*l*) surface by the micropores of MS3A (0.3 nm) is essential for C₂H₆ 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 C₂H₆. 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.

Acknowledgements

This work was supported by JST-CREST projects (Grant Number JPMJCR15P4).

References

- 1 P. Schwach, X. Pan and X. Bao, *Chem. Rev.*, 2017, **117**, 8497–8520.
- 2 G. E. Keller and M. M. Bhasin, *J. Catal.*, 1982, **73**, 9–19.
- 3 T. Ito and J. H. Lunsford, *Nature*, 1985, **314**, 721–722.
- 4 K. Otsuka, K. Jinno and A. Morikawa, *Chem. Lett.*, 1985, 499–500.
- 5 L. Wang, L. Tao, M. Xie, G. Xu, J. Huang and Y. Xu, *Catal. Lett.*, 1993, **21**, 35–41.
- 6 X. Guo, G. Fang, G. Li, H. Ma, H. Fan, L. Yu, C. Ma, X. Wu, D. Deng and M. Wei, *Science*, 2014, **344**, 616–619.
- 7 Y. Nishikawa, H. Ogihara and I. Yamanaka, *ChemistrySelect*, 2017, **2**, 4572–4576.
- 8 A. L. Dipu, S. Ohbuchi, Y. Nishikawa, S. Iguchi, H. Ogihara and I. Yamanaka, *ACS Catal.*, 2020, **10**, 375–379.
- 9 Y. Ohtsuka, Y. Nishikawa, H. Ogihara, I. Yamanaka, A. Nakayama and J. Hasegawa, *J. Phys. Chem. A*, 2019, **123**, 8907–8912.
- 10 U. Kashaboina, Y. Nishikawa, Y. Wakisaka, N. Sirisit, S. Nagamatsu, D. Bao, H. A. Miwa, S. Takakusagi, Y. Inami, F. Kuriyama, A. L. Dipu, H. Ogihara, S. Iguchi, I. Yamanaka, T. Wada and K. Asakura, *Chem. Lett.*, 2019, **48**, 1145–1147.
- 11 Y. Nishikawa, Y. Ohtsuka, H. Ogihara, R. Rattanawan, M. Gao, A. Nakayama, J. Hasegawa and I. Yamanaka, *ACS Omega*, 2020, **5**, 28158–28167.
- 12 W. Fan, S. Shirato, F. Gao, M. Ogura and T. Okubo, *Microporous Mesoporous Mater.*, 2006, **89**, 227–234.
- 13 R. Abid, G. Delahay and H. Tounsi, *J. Mater. Cycles Waste Manage.*, 2019, **21**, 1188–1196.