Selective Conversion of Methane to Ethane and Hydrogen over In/Molecular-Sieve-3A Catalyst

Journal:	*Catalysis Science & Technology*
Manuscript ID	CY-ART-09-2023-001217.R1
Article Type:	Paper
Date Submitted by the Author:	14-Oct-2023
Complete List of Authors:	Nakaya, Ayumi; Tokyo Institute of Technology School of Materials and Chemical Technology , Department of Chemical Science and Engineering Suzuki, Ayako; Tokyo Institute of Technology School of Materials and Chemical Technology , Department of Chemical Science and Engineering Iguchi, Shoji; Tokyo Institute of Technology School of Materials and Chemical Technology , Department of Chemical Science and Engineering Yamanaka, Ichiro; Tokyo Institute of Technology, Chemical Science and Engineering

Selective Conversion of Methane to Ethane and Hydrogen over In/Molecular-Sieve-3A Catalyst

Ayumi Nakaya[1], Ayako Suzuki[1], Shoji Iguchi[1,2], Ichiro Yamanaka[1]*

1. Department of Chemical Science and Engineering, Tokyo Institute of Technology, Ookayama 2-12-1-S1-16, Meguro, Tokyo, 152-8552, Japan.
2. Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto, 615-8510, Japan.

Abstract

Direct conversion of methane to valuable chemicals is attractive subject. 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 has been reported. The In catalyst showed an excellent catalysis for the DCM reaction and selective formation of ethane and hydrogen without carbon deposition at lower temperature of 873 K in this work. Catalytic activity of In strongly depended on supports at 873 K and 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. Function of the MS3A support in the DCM reaction was discussed.

1. Introduction

Conversion of CH_4 as a major component of natural gas into useful chemicals is one of the hot topics to solve the depletion of oil. Now, CH_4 is used for a source of thermal energy and electric power. Except for methanol synthesis and Fischer-Tröpsh process, we do not have catalytic technology for direct conversion of CH_4 into useful chemicals. Study in new catalysts and reactions are essential for developing the direct conversion process of CH_4.

A large number of chemists has been studying catalysts and reactions for the conversion of CH_4; however, strong C-H bonds of CH_4 and a symmetric molecular form are essential problem for activation of CH_4 [1]. Two scientific fields of pioneering works have been reported, one is oxidative coupling of CH_4 (OCM) to C_2H_6 and C_2H_4 with O_2 [2-4] and the other is dehydrogenative conversion of CH_4 (DCM) or none oxidative coupling of CH_4 (NOCM) to higher hydrocarbons [5-8]. In the later field, most of all works have focused on catalysis of transition metal elements (Mo, Fe, Ni etc.) because of their strong catalysis on activation of C-H bonds, whereas we focused on post-transition metal elements (Ga, In, Bi, Sn) because of their mild catalysis on activation of C-H bonds. Especially, 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 of 70% of selectivity to sum of hydrocarbons (ethylene, ethane, propylene, benzene toluene) with 4% conversion of CH_4 at 1173 K. The particular nature of the In/SiO_2 catalyst is that metal liquid of In shows catalysis for the activation of CH_4. This unique property of In metal liquid for the DCM reaction have been studied by kinetic studies, isotope effects studies, first-principle DFT MD calculations [9] and XAFS observation [10]. The major conclusions of our previous papers follow; (i) In metal liquid is thermally activated, (ii) the activated In species, In-In cluster model, can cleave a C-H bond of CH_4 to CH_3-In and H-In species, then couplings of two CH_3-In species produce C_2H_6 and of two H-In species produce H_2, and (iii) onset temperature of activation of CH_4 by In liquid metal is observed around 850 K by temperature programed reaction (TPR) studies using mass spectra analysis, but a quantitative analysis could not be done [11].

In this paper, we have found that In catalyst showed significant catalytic activity for the DCM reaction at a lower temperature of 873 K and support materials strongly affected the In catalysis; especially, molecular sieve 3A (MS3A) was effective. Aims of this work are to clarify effects of MS3A support on In catalysis at around 873 K and to propose function of MS3A support to enhance the catalytic activity of 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 catalyst preparations (Supporting Information). The SiO_2 support was added in deionized water dissolved $In(NO_3)•nH_2O$, and this mixture was strongly mixed by a magnetic spin-bar. The suspension was dried up 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 for 3 h at 1173 K, the In/SiO_2 catalysts were obtained. A loading of In^0 was 10 wt%.

In/MS3A catalyst was prepared as similar way to the In/SiO_2 catalyst. Different procedures were calcination of MS3A (Wako Pure Chemical Industries) at 1023K and reduction of InOx/MS3A with H_2 at 1023 K. A loading of In^0 was the same as 10 wt%.

We prepared different type of In/MS3A catalyst as follows, the catalyst precursor of InOx/MS3A was hold in saturated water-vapor at 45 ˚C. This humidified InOx/MS3A material was reduced with pure H_2 at 1173 K as the same reduction procedure of the In/SiO_2 and In/MS3A catalysts. The prepared catalyst was called as In/MS3A(humid). As 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 (Figure S1). After Ar flowed through the reactor to replace air, H_2 flowed with 20 mL min^{-1} and temperature raised with 25 K min^{-1} to 873K holding 60 min. Then reduction temperature raised to 1023K and lowered to reaction temperature. After H_2 was replaced with Ar for 60 min, CH_4 flowed with 10 mL $min^{-1}$and the DCM rection started [7,8, 11].

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

$$\mathrm{CH_4\ conversion} = \frac{2*\mathrm{FR}(\mathrm{H_2})+6*\mathrm{FR}(\mathrm{C_2H_6})+4*\mathrm{FR}(\mathrm{C_2H_4})}{2*\mathrm{FR}(\mathrm{H_2})+6*\mathrm{FR}(\mathrm{C_2H_6})+4*\mathrm{FR}(\mathrm{C_2H_4})+4*\mathrm{DR}(\mathrm{CH_4})} \times 100\ (\%) \qquad \text{eq. 1}$$

$$\mathrm{C_2H_6\ selectivity} = \frac{8*\mathrm{FR}(\mathrm{C_2H_6})}{2*\mathrm{FR}(\mathrm{H_2})+6*\mathrm{FR}(\mathrm{C_2H_6})+4*\mathrm{FR}(\mathrm{C_2H_4})} \times 100\ (\%) \qquad \text{eq.2}$$

$$\mathrm{C_2H_4\ selectivity} = \frac{8*\mathrm{FR}(\mathrm{C_2H_4})}{2*\mathrm{FR}(\mathrm{H_2})+6*\mathrm{FR}(\mathrm{C_2H_6})+4*\mathrm{FR}(\mathrm{C_2H_4})} \times 100\ (\%) \qquad \text{eq.3}$$

(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 Discussions

3.1 Catalysis of In(*l*) at a lower temperature

As mentioned in the introduction, the previous result of the temperature-programed-reaction study equipped a mass spectrometer for CH_4 conversion on the In/SiO_2 catalyst suggested that activation of C-H bonds of CH_4 would proceed at a lower temperature around 850 K than 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 formation of products or not at 873 K by the GC analysis.

Figure 1 shows time courses of formations 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 were confirmed at 873 K. The formation rate of C_2H_6 gradually decreased with process time until 120 min and steady formation was observed after 150 min. A formation rate of H_2 gradually decreased as similar to that of C_2H_6. The formation rates of C_2H_6 were lower than these of H_2 for 120 min. In contrast, the both formation rates were almost equal after 150 min until 240 min. The changing in formation rates reflected on the selectivity to C_2H_6 as plotted in Figure 1. In a first half until 120 min, an apparent selectivity to C_2H_6 were about 95% and the selectivity were almost 100% in a second half after 180 min. Stoichiometric conversion of CH_4 to C_2H_6 and H_2 continuously proceeded after 180 min (eq 4). The selectivity below 100% means that un-identified hydrocarbon or carbon deposition form (eq 5). The average results during 180 min were indicated in run 1 of Table1.

$$2CH_4 \rightarrow C_2H_6 + H_2 \qquad \Delta H^0 = +66 \text{ kJ mol}^{-1} \qquad \text{eq. 4}$$

$$CH_4 \rightarrow C_{(s)} + 2H_2 \qquad \Delta H^0 = +75 \text{ kJ mol}^{-1} \qquad \text{eq. 5}$$

When a In_2O_3/SiO_2 material as a precursor of the In/SiO_2 catalyst before the reduction, was applied for the DCM reaction, a lower formation rate of C_2H_6 and a higher formation rate of H_2 were observed at run 2 in Table 1. This clearly indicated that In^0(*l*) was active phase for the selective C_2H_6 formation at a lower temperature of 873 K and SiO_2 (CARiACT Q-3) was 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 at runs 3-8 in Table 1. All oxide supports were calcined in air at 1173 K before the preparation of In/oxide support catalysts. Formation rates of C_2H_6 and H_2 were strongly affected by the oxide supports. In the case of CeO_2 and MgO supports, formation rates of C_2H_6 were enhanced but that of H_2 was strongly accelerated. Other supports, Al_2O_3, TiO_2, Nb_2O_5, ZrO_2, formation rates of C_2H_6 were suppressed and the decomposition rates were accelerated. Excess formation of H_2 was due to decomposition of CH_4 to carbon deposition 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 over 95% selectivity to C_2H_6 and H_2 at 873 K. In order to clarify nature of SiO_2 support for the DCM reaction, three SiO_2 materials, CARiACT Q-30, Admafine SO-E6, AEROSIL 300, were tested for the support. All SiO_2 materials calcined in air at 1173 K before the procedure of impregnation of $In(NO_3)_3$ as mentioned in the experimental section. Figure 2 shows relationship between formation rates of C_2H_6 and specific surface areas of SiO_2 supports calcined at 1173 K.

As you can see clearly in Figure 2, a SiO_2 support having a lower surface area was suitable for 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 $In^0(l)$ catalyst at 873 K.

We have already reported 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]. Brief reaction mechanism is as follows; (i) In liquid metal catalyzes activation of C-H bond of CH_4, (ii) CH_3-In(l) and H-In(l) species produce, then (iii) two CH_3-In(l) species on the liquid surface couple and produce C_2H_6, (iv) H species on In diffuse into a bulk phase of In(l), (v) two H species dissolved in the bulk In(l) are coupled at the surface and desorb as H_2.

When a SiO_2 support having a lower surface area, 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 having higher surface area, 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 atoms by surface catalysis of SiO_2. If this mechanism was true, 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 a high selectivity to conversion of CH_4 to C_2H_6 and H_2; however, the conversion of CH_4 in Figure 1 was only 0.004% which calculated from product yields by GC (eq. 1). The thermodynamic equilibrium conversion of this reaction is about 0.9% at 873 K. We have considered that the formation rate of C_2H_6 through coupling of CH_3 species was suppressed by equilibrium between CH_3 species and H species on the surface of $In^0(l)$ [11]. In other words, if we could accelerate elimination of H species from the surface of $In^0(l)$, 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 come up an idea for the acceleration. Our idea is utilization of function of molecular sieve for the elimination of H species, that is to separate CH_3 and H species by function of molecular sieve. A molecular sieve-3A (MS3A) has micro-pore about 0.3 nm in which H species can introduce into the micro-pore but CH_4 and maybe CH_3 species could not. If this anticipation idea comes true, H species on and in $In^0(l)$ be spillover and diffuse to the MS3A and coupling reaction of CH_3 species to C_2H_6 accelerate.

In/MS3A catalyst was prepared by impregnation method as resemble to the preparation method of the In/SiO_2 catalyst. The MS3A support was calcined in air at 1023 K before the preparation of catalyst, as described in the experimental section. The catalytic activity of In/MS3A at 873 K was indicated in run 9 of Table 2. As you can see clearly to compare runs 1 and 9, formation rate of C_2H_6 on the In/MS3A catalyst significantly accelerated 5 times higher than that of 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 selectivity to sum 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 preparation conditions of the catalyst, calcination temperatures and times, reduction temperatures and times, partial pressure of H_2 and temperature for the reduction, etc. Then we have found humidity around the catalyst precursor, InOx/MS3A, influenced the catalytic activity of the In/MS3A catalyst and this was named as In/MS3A(humid). Preparation procedures were mentioned in the experimental section. As shown at run 10, the formation rate of C_2H_6 accelerated 1.4 times by the humidifying treatment and the selectivity to sum of C_2H_6 and C_2H_4 was 104% calculated from eq.2. The selectivity over 100% indicated less formation of H_2 to compare with hydrocarbon formation. As a reference, a In/SiO_2(humid) catalyst was applied for the DCM reaction. As indicated at run 11, a little acceleration of C_2H_6 formation was observed by the humidified treatment of InOx/SiO_2.

To reveal 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 through the above procedures and the results were indicated at run 12 and 13 in Table 2, respectively. No accelerations for the C_2H_6 formation rate by the MS4A and LTA supports were clear to compare the data among the runs 10-13. In addition, the selectivity to C_2H_6 decreased by 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 in runs 10, 14-16. 5 wt% In/MS3A(humid) catalyst showed a lower formation rate of C_2H_6 and a good one of H_2, corresponding to a lower selectivity to C_2H_6. 20 wt% In/MS3A(humid) catalyst showed a highest catalytic activity and a highest selectivity to sum of C_2H_6 and C_2H_4 over 100%.

Time courses of sun formation of C_2H_6 and C_2H_4 on the In/MS3A(humid), In/MS4A(humid) and In/SiO_2(humid) catalysts were indicated in Figure 3. The formation rate of sum of C_2H_6 and C_2H_4 over the In/MS3A(humid) catalyst was far higher than that over the In/SiO_2(humid) catalyst at initial stage of the reaction and decreased with process time. However, significant acceleration of C_2H_6 formation on the In/MS3A(humid) catalyst was observed at 180 min. The selectivity to C_2H_4 were constant during the reaction; 7 % on the In/MS3A(humid), 3% on the In/MS4A(humid) and In/SiO_2(humid) catalysts.

Figure 4 shows effects of reaction temperatures on (a) formation rate of sum of C_2H_6 and C_2H_4 and (b) their selectivity on the 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 don't work. In addition, the In/MS3A(humid) catalyst showed catalytic activity even at 723 K though a lower selectivity. An advantage of In/MS3A(humid) catalyst against the In/MS4A(humid) and In/SiO_2(humid) catalysts for activation and conversion of CH_4 was clear. Apparent activation energies over the In/MS3A(humid), In/MS4A(humid) and In/SiO_2(humid) catalysts were calculated by Arrhenius plots and were 16.2, 15.4 and 20.6 kJ mol^{-1}, respectively (Figure S2). These apparent activation energies were too low to compare the cleavage energy of 463 kJ mol^{-1} in 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 temperature over 1000 K. In other words, 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.

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

4. Discussion

Basic characterization studies for In/MS3A(humid), In/MS4A(humid) and In/SiO_2(humid) catalysts were conducted by XRD and N_2 adsorption measurements. Figure 5 shows XRD patterns of the three catalysts. Diffraction patters of In^0 were clearly observed for the three catalysts. Original diffraction patterns identified 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 were 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 calcination at 1023K. These observations suggest that original crystal structures of MS3A and MS4A are decomposed by the calcination; however, part of original pores of MS3A and MS4A would remain after the calcination. Therefore, we can observe differences in catalytic activities among the In/MS3A(humid), In/MS4A(humid) and In/SiO_2(humid) catalysts for the DCM reaction.

Effective pore diameters of original MS3A, MS4A and LTA materials were 0.3, 0.4 and 0.5 nm, respectively. As mentioned above, we raised the idea of separation of CH_3 and H species by function of molecular sieve. The micro-pore of MS3A as 0.3 nm in which H species (< 0.3 nm) can introduce but CH_4 (3.8 nm) and maybe CH_3 species cannot. If this model is true, the recombination of CH_3 species and H species is suppressed and coupling 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 Figure 3 and Table 2. We consider that separation of H and CH_3 species on the In(*l*) surface by micro-pores of MS3A (0.3 nm) is essential for C_2H_6 formation, as described above. We speculate that H species accumulate in the micro-pores and acceleration of H species removal in the micro-pores is essential to enhance the formation rate of C_2H_6. We have plane to prove the accumulation of hydrogen species in micro-pores of the In/MS3A(humid) catalyst by applying TPD experiments as future work.

Acknowlagement

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

References

[1] P. Schwach. X. Pan, X. Bao, Chem. Rev. **2017**, 117, 8497-8520.

[2] G. E. Keller, M. M. Bhasin, J. Catal. **1982**, 73, 9-19.

[3] T. Ito, J. H. Lunsford, Nature, **1985**, 314, 721-722.

[4] K. Otsuka, K. Jinno, A. Morikawa, Chem. Lett. **1985**, 499-500.

[5] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang, 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, M, Wei, Science, **2014**, 344, 616-619.

[7] Y. Nishikawa, H. Ogihara, I. Yamanaka, ChemistrySelect **2017**, 2, 4572-4576.

[8] A. L. Dipu, S. Ohbuchi, Y. Nishikawa, S. Iguchi, H. Ogihara, I. Yamanaka, *ACS Catalysis*, **2020**, 10, 375−379.

[9] Y. Ohtsuka, Y. Nishikawa, H. Ogihara, I. Yamanaka, A. Nakayama, 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, K. Asakura, Chem. Lett. **2019**, 48, 1145-1147.

[11] Y. Nishikawa, Y. Ohtsuka, H. Ogihara, R. Rattanawan, M. Gao, A. Nakayama, J. Hasegawa, I. Yamanaka, *ACS Omega* **2020**, 5, 28158−28167.

[12] W. Fan, S. Shirato, F. Gao, M. Ogura, T. Okubo, Microp. & Mesop. Materials **2006,** 89 227–234

[13] R. Abid, G. Delahay, H. Tounsi, J. Mat. Cycl. Wast. Management, **2019**, 21, 1188-1196.

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

Run	Catalyst	Form. rate / µmol min^{-1} g-cat^{-1}		Select. / %
		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.

Table 2. Results of the DCM reaction by In/Molecular-Sieve catalysts at 873 K.

Run	Catalyst	Format. rate / µmol min^{-1} g-cat^{-1}			Select. / %
		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.

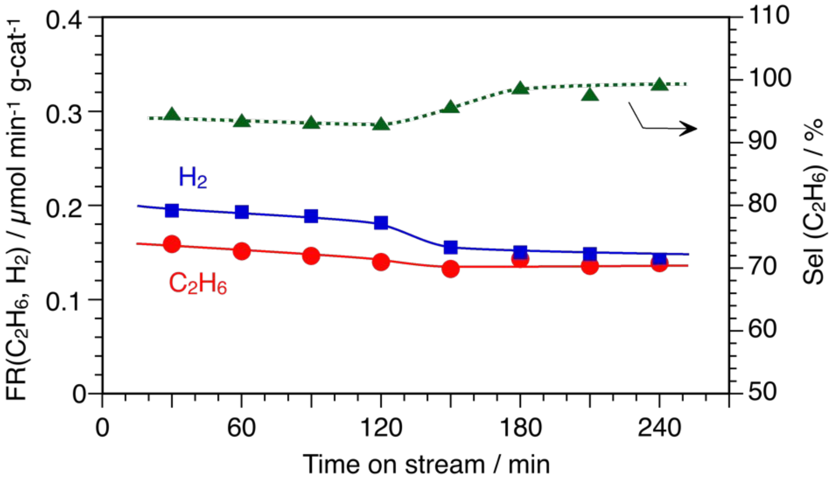

Figure 1. Time courses of DCM reaction by In/SiO_2 catalyst at 873 K.

CH_4: 1 atm and 10 mL min^{-1}, catalyst: 10 wt% In/SiO_2

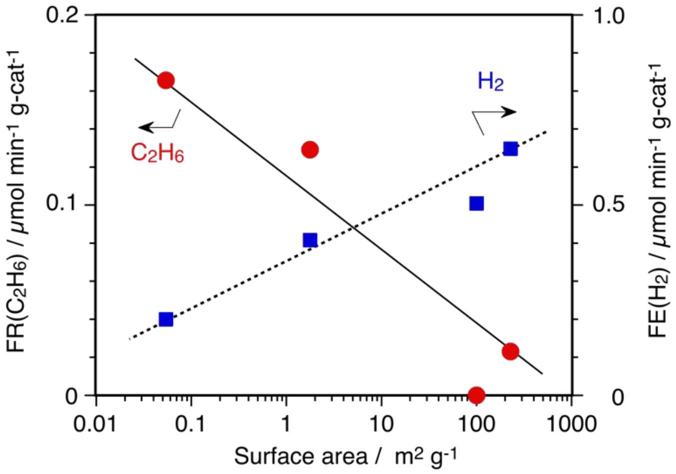

Figure 2. Influence of surface area of SiO_2 support on DCM reaction by 10 wt% In/SiO_2 catalysts at 873 K. Amount of catalyst 100 mg, CH_4: 1 atm and 10 mL min^{-1}.

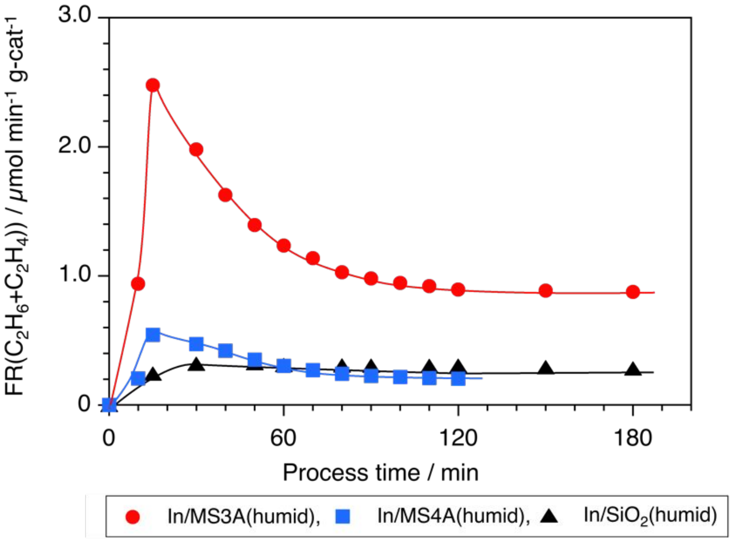

Figure 3. Time courses of formation rate of the sum of C_2H_6 and C_2H_4 by 10 wt% In/MS3A(humid), 10% In/MS4A(humid) and 10 wt% In/SiO_2(humid) catalysts.

Amount of catalyst 100 mg, CH_4: 1 atm and 10 mL min^{-1}.

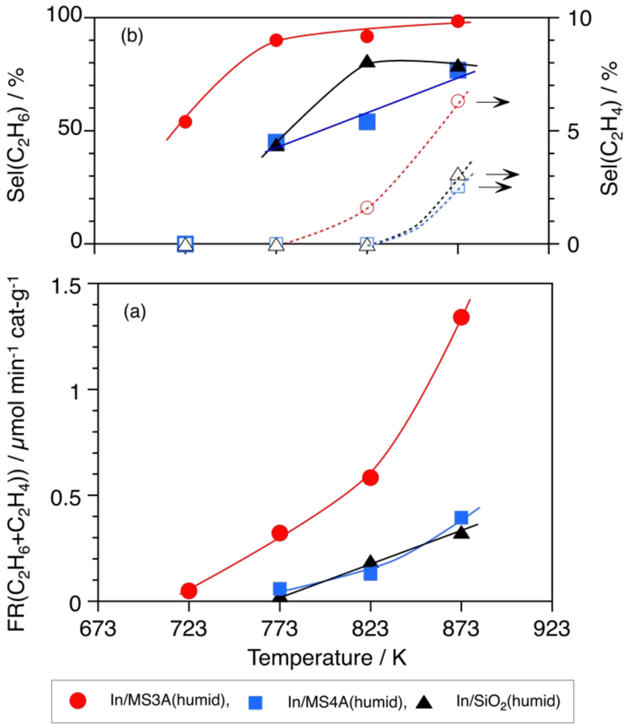

Figure 4. Effects of reaction temperatures on the DCM reaction by 10 wt% In/MS3A(humid), 10% In/MS4A(humid) and 10 wt% In/SiO_2(humid) catalysts, (a) formation rate of sum of C_2H_6 and C_2H_4, (b) selectivity to C_2H_6 and C_2H_4. Amount of catalyst 100 mg, CH_4: 1 atm and 10 mL min^{-1}.

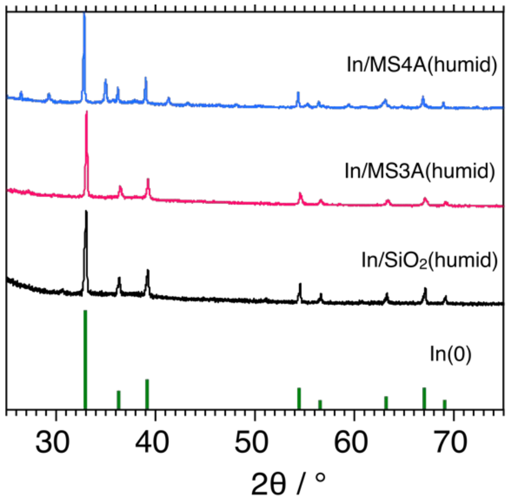

Figure 5. XRD patterns of 10 wt% In/MS3A(humid), 10% In/MS4A(humid) and 10 wt% In/SiO_2(humid) flesh catalysts.