

Selective Propene Synthesis from Ethene without Metathesis on Silica Supported Cobalt Catalyst

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Selective chain propagation of ethene to propene (ETP reaction) was made on silica supported cobalt (Co/SiO₂) catalyst. It was suggested that the proper conditions for the chain propagation reaction were close to those for the Fischer-Tropsch reaction. When an equimolecular mixture of ¹²C₂-C₂H₄ and ¹³C₂-C₂H₄ was contacted on the catalyst, inter-molecular exchange of methylidene, ¹²C₂-C₂H₄ + ¹³C₂-C₂H₄ \rightleftharpoons 2¹³C₁-C₂H₄, namely, metathesis, was not occurred in the ETP reaction. And as a result, the selective chain propagation of ethene to propene without metathesis was successfully achieved on Co/SiO₂ catalyst.

Keywords: cobalt based catalyst, chain propagation, olefin metathesis, olefin homology, ETP reaction.

1. INTRODUCTION

Selective chain propagation of ethene to propene, namely ETP reaction (3C₂H₄ → 2C₃H₆), has been investigated on MoO_x/SiO₂, WO_x/SiO₂, and so on¹⁻⁴, which are active for the olefin metathesis reaction (R₁R₂C=CR₁R₂ + R₃R₄C=CR₃R₄ → 2R₁R₂C=CR₃R₄)³⁻⁵. It has been, therefore, putatively accepted that the ETP is analogous reaction of the metathesis.

However, the synthesis of propene is recently demonstrated on Ni/MCM-41 catalyst. It is caused by reverse metathesis (C₂H₄ + C₄H₈ → 2C₃H₆) following the dimerization of ethene and the isomerization of 1-butene to 2-butene⁶, e.g., the propene is not obtained by directive chain propagation of ethene on it.

In contrast to this, it is suggested that the directive ETP reaction proceeds via bridged alkylidene and metallacyclic species on iron based catalyst showing activity for Fischer-Tropsch (FT) synthesis (n CO + (n + m/2) H₂ → C_nH_m + nH₂O)⁷. So far, several trials to clarify a difference of active sites for the ETP reaction and the olefin metathesis were made on supported molybdena catalysts. Olefin metathesis reaction proceeds on molybdena species which have higher oxidation state such as MoO_y (Y around 2.9) whereas the ETP reaction does not occur at all on it⁸. In addition both the metathesis and the ETP were promoted by reduced molybdena species (MoO_x; X around 2.2)^{3,4}. These facts may suggest that olefin metathesis active catalyst is not always active for the ETP, but that ETP active catalyst also promotes the metathesis.

However, certain evidence for inverse phenomenon, that is, the selective ETP without the metathesis on heterogeneous catalyst almost can not be seen at the present time. In this study, selective ETP without metathesis was demonstrated on silica supported cobalt (Co/SiO₂) catalyst by using ¹³C labeled ethene as a tracer.

2. EXPERIMENTAL

Preparation of Co/SiO₂ catalyst:

Aqueous solution of cobalt nitrate (II) hexahydrate (Co(NO₃)₂·6H₂O, GR, Kanto Chemical) was immersed

into a silica (Silica gel 60, Merck) with a surface area of 410m²/g. Loading amount of cobalt relative to the whole catalyst weight was varied from 0 to 20 wt.%. The slurry was aspirated to remove water at 55 °C for several hours and it was further calcined at 520 °C in air for 3 h. The catalyst (0.5 g) was evacuated in the order of 10⁻² Pa at 500 °C for 1 h before the reduction. Then the specimen was activated by reduction with hydrogen (ca. 26.7 kPa) at 500 °C for 1 h. Finally, it was evacuated again at 500 °C for 1 h prior to the ETP and the metathesis reactions. For instance, hereinafter the catalyst containing 10 wt.% of Co was simply denoted as Co(10)/SiO₂.

MoO_x/SiO₂ catalyst:

The catalyst was prepared by the analogous procedure as mentioned above except using ammonium paramolybdate ((NH₄)₆Mo₇O₂₄·6H₂O, GR, Wako Chemical) instead of cobalt nitrate. The loading amount of MoO₃ was set at 7 wt.% which is reported as proper concentration for the ETP and the metathesis⁴.

Reactions:

In order to evaluate the ETP, 6.7 kPa of ethene (99.5% purity, Taiyo Nissan Co.) was introduced on 0.5 g of virgin catalyst. To confirm simultaneously the activity of metathesis and that of ETP, 6.7kPa of an equimolecular mixture of ¹²C₂-C₂H₄ and ¹³C₂-C₂H₄ (Isotec Inc. USA, 99 atom% purity of ¹³C) was used. Catalyst activation and the reactions were carried out in closed glass circulation system with a volume of 390ml. The composition of propene in gas phase for the ETP and that of ¹³C₁-C₂H₄ for the metathesis were determined by a FID gas chromatograph (Shimadzu, GC-14B) equipped with a stainless steel column which was packed with VZ-10 (GL Science) and a quadrupole mass spectrometer (Pfeiffer Prisma, QMS-200), respectively.

3. RESULTS AND DISCUSSION

ETP reaction on Co/SiO₂ catalyst:

Fig. 1 shows composition of propene at 120 min as a function of reduction temperature of Co(10)/SiO₂

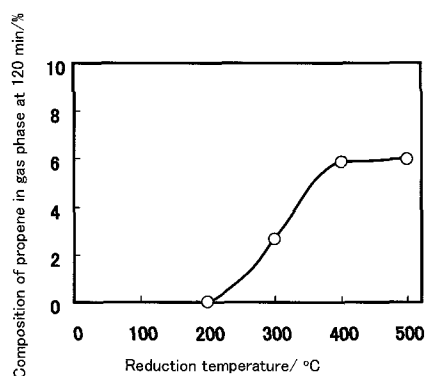


Figure 1. Propene formation from ethene as a function of reduction temperature of Co(10)/SiO₂ catalyst.

P_{C₂H₄}: 6.7kPa, Reaction temperature: 260°C, Catalyst weight: 0.5g.

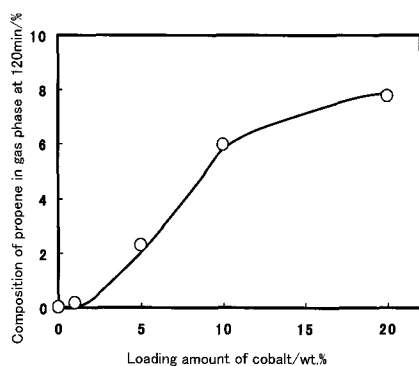


Figure 2. Propene formation as a function of loading amount of cobalt in Co/SiO₂ catalyst.

Reaction conditions were the same as in Fig. 1.

catalyst when the reaction temperature was set at 260 °C. The infinitesimal ETP activity was appeared on the catalyst reduced at 200 °C and the activity was increased significantly on the catalyst reduced at 400 °C.

Upon raising the reduction temperature to 500 °C, the activity was almost the same on the catalyst reduced at 400 °C. It has been demonstrated that the ETP takes place on the deeply reduced MoO_x/SiO₂^{3,4)} and that the FT synthesis proceeds on cobalt based catalyst reduced around 400 °C⁹⁾. Hence it might be considered that the active sites for the ETP on Co/SiO₂ was formed during reduction over ca. 400 °C which may have low oxidation state as well as those for the FT synthesis.

It is reported in supported cobalt catalyst system that the activity for the FT synthesis appears chiefly in the range of loading amount between ca. 10 and ca. 20 wt. %⁹⁾. If this fact for the FT is also worthy for the ETP involving chain propagation, it is expected that the ETP reaction will readily proceed on Co(10~20)/SiO₂ catalysts.

Fig. 2 shows the composition of propene in gas phase as a function of loading amount of cobalt. Examined catalysts were reduced at 500 °C and the ETP was carried out at 260 °C. When the silica (support) was used individually, no formation of propene was recognized. Varying the loading amount of cobalt, formation of propene from ethene was increased significantly until

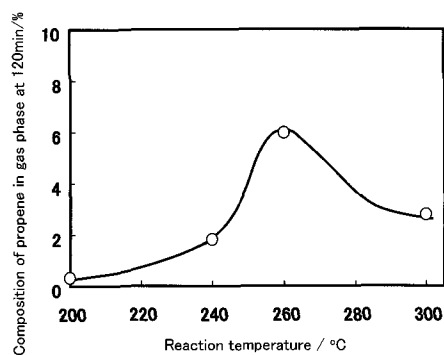


Figure 3. The ETP reaction on Co(10)/SiO₂ catalyst at various temperature.

Reaction conditions were the same as in Fig. 1, except changing reaction temperature.

the loading amount was reached 10 wt.%. Further increasing the loading amount from 10 to 20 wt.%, the formation of propene was still increased from ca. 6 to ca. 8%. Therefore it could be confirmed that the proper loading amount for the ETP was laid near 10 wt.% or slightly more.

When the reaction temperature was changed from 200 to 300 °C, the produced amount of propene was very small at 200 °C and it was increased by raising

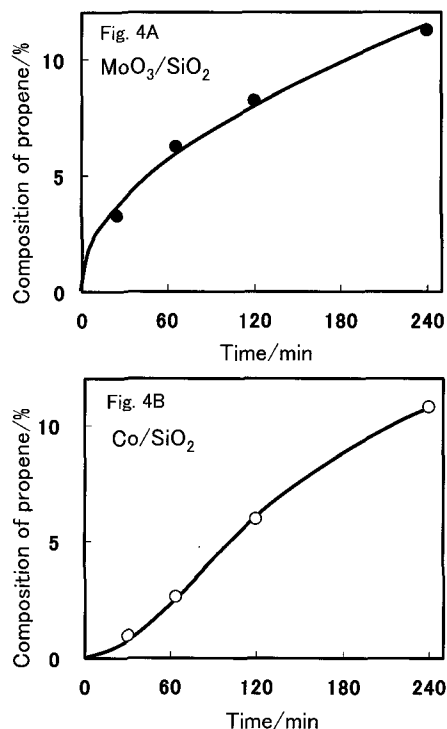


Figure 4. Propene formation on MoO₃/SiO₂, and Co(10)/SiO₂ catalysts at 260 °C.

Reaction conditions were the same as in Fig. 1 except using a 1 : 1 mixture of ¹²C₂-C₂H₄: ¹³C₂-C₂H₄. Loading amount of MoO₃ was 7 wt.%. In working state of the catalyst, X of MoO_x was around 2.2, which was almost the same as in the refs^{3,4)}.

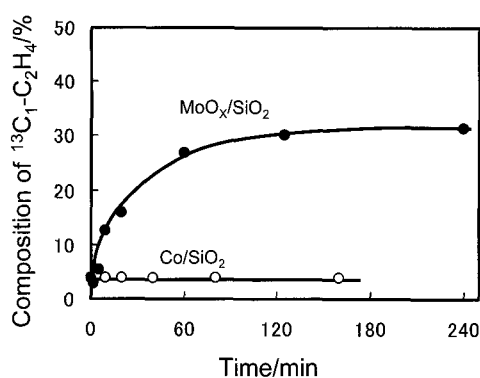


Figure 5. Ethene metathesis in the ETP reaction on MoO₃/SiO₂(●), and Co(10)/SiO₂ (○) catalysts at 260 °C. Reaction conditions were the same as in Fig. 4. The ETP and ethene metathesis were simultaneously carried out.

temperature. The fraction was reached maximum (6% after 120 min) at 260 °C on Co(10)/SiO₂ catalyst as shown in Fig. 3. In the commercial FT process, the diesel gas oils, naphtha, etc. are obtaining in the process operated around 220 ~ 250 °C^{10, 11}). Thus a part of the proper reaction temperature range for the ETP was overlapped on that for the FT synthesis.

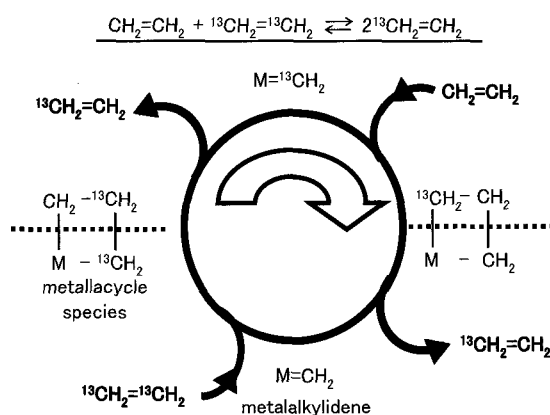
It was very interesting that the reduction temperature, loading amount of cobalt species, and reaction temperature for the ETP were close to those for the FT synthesis.

In FT active catalysts, for example, it is suggested that the bridged carbene is closely related to promote the chain propagation steps⁷). On the other hand, the linear carbene is generally accepted for one of important species for the olefin metathesis¹²). In addition, it is conjectured that MoO_x/SiO₂ catalyst may provide linear and bridged carbene species on the surface^{12, 13}). If the Co/SiO₂ catalyst preferentially gives bridged carbene species, a possibility to promote the selective chain propagation of ethene to propene without the olefin metathesis will be realized.

These expectations led me to confirm whether the selective ETP without the metathesis was occurred on the Co/SiO₂ or not.

Ethene metathesis in ETP on Co/SiO₂ and MoO_x/SiO₂ catalysts:

In order to compare simultaneously the activity of the ethene metathesis and the ETP reaction, an equimolecular mixture of ¹²C₂-C₂H₄ and ¹³C₂-C₂H₄ was used as a reactant. When an equimolecular mixture of ¹²C₂-C₂H₄ and ¹³C₂-C₂H₄ was introduced onto MoO_x/SiO₂ catalyst at 260 °C, propene was produced by the ETP reaction and the composition of propene (●) was reached 11.5 % after 240min as described in Fig. 4A. Upon contacting the gas mixture onto Co(10)/SiO₂ catalyst as the same way, propene was obtained and its composition was very close to the case using MoO_x/SiO₂ catalyst as in Fig. 4B (○). So far, it is known that MoO_x/SiO₂ catalyst has high activity for the ETP reaction. The result suggested that the Co/SiO₂ has also considerable activity for the ETP as well as MoO_x/SiO₂



Scheme 1. Mechanism of catalytic ethene metathesis reaction via metalalkylidene and metallacycle species.

catalyst.

It has been considered that olefin metathesis reaction proceeds through metalalkylidene and metallacycle species in homogeneous and heterogeneous catalyst systems^{1, 8, 13, 14}). Therefore, if the ethene metathesis is occurred on a catalyst, ¹³C₁-C₂H₄ will be formed through the reaction path as shown in Scheme 1. Fig. 5 shows formation of ¹³C₁-C₂H₄ in the ETP reaction on MoO_x/SiO₂ and Co(10)/SiO₂ catalysts. ¹³C₁-C₂H₄ was reached ca. 30 % after 120 min (●), thus, it was confirmed that the ethene metathesis reaction rapidly proceeded on MoO_x/SiO₂. In contrast to the result in the MoO_x/SiO₂, content of ¹³C₁-C₂H₄ in gas phase was kept around 4.5 % even at 160 min (○). The small amount of ¹³C₁-C₂H₄ was existed in the ¹³C₂-C₂H₄ as an impurity. The result clearly indicated that the ethene metathesis was suppressed completely on Co/SiO₂ catalyst in the ETP reaction.

It could be concluded, at least, from these results that the ETP reaction was taken place alone on Co/SiO₂ catalyst without metathesis. This may be the first demonstration that the catalyst which has an activity for the ETP reaction was not always active for the olefin metathesis in the inorganic heterogeneous catalyst system. Author may expect that the technique will throw light upon the rationalized production of propene synthesis.

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