Enhancement of Propene Formation by Co-feeding Ethene and Synthesis Gas on Co/SiO₂ Catalyst

Takashi SUZUKI
Gunma Prefectural Industrial Technology Center, 884-1, Kamesato, Maebashi 379-2147, Japan

Trial to synthesize propene from ethene was carried out on silica supported cobalt (Co/SiO₂) catalyst by using slurry bubble column reactor. Catalytic propene formation was recognized on that catalyst. When a gas mixture of ethene and synthesis gas (syngas), which is 1:2 mixture of carbon monoxide and hydrogen was fed onto Co/SiO₂ catalyst, the produce rate of propene was increased 4-fold as much as that in the case flowing ethene alone. It was conjectured that the enhancement of propene formation in the presence of ethene and syngas was caused by increase methyldiene (=CH₂) species which was readily reacted with ethene to form propene.

**Keywords:** Synthesis of propene, ETP reaction, Olefin homologation, Olefin metathesis, Co/SiO₂ catalyst.

1. INTRODUCTION

Considerable amount of polyolefin such as polypropylene which is one of environmentally harmonized materials has been widely applied to make various products. Thus the demand of propene increases in petrochemical industry. Therefore development of rationalized production of ethene is expected from the industrial viewpoint. Chain propagation of ethene to propene (3C₂H₄ → 2C₃H₆), namely ETP is a reaction to yield the olefin having much one of the carbon number in comparison with the original olefin. So far, trials of ETP reaction have been made on MoOX/SiO₂, WOX/SiO₂, and so on, which have been known to have catalytic activity for the olefin metathesis reaction (R₁R₂C=CR₂R₁ + R₃R₄C=CR₄R₃ → 2R₁R₃C=CR₂R₄, 2R₁R₄C=CR₃R₂).

Recently, three step synthesis of propene from ethene is suggested on Ni/MCM-41 catalyst. In the catalyst system, propene is produced by reverse metathesis (C₃H₆ + C₄H₈ → 2C₂H₆) following the dimerization of ethene and the isomerization of 1-butenes to 2-butenes.

In contrast to these, it is observed on Fe/SiO₂ catalyst which is prepared by using iron carbonyl compounds as precursor that the direct synthesis of propene from ethene may proceed via bridged alkylidene and metallacyclic intermediates around 200°C under atmospheric pressure. It is pointed out that metallacyclic species have important role in the olefin metathesis. The supported iron catalyst also promotes Fischer-Tropsch (FT) synthesis (nCO + (n + m/2)H₂ → CₙH₂ₙ₊₁ + n H₂O).

Author suggests that the ETP reaction proceeds without the olefin metathesis on Co/SiO₂ catalyst which shows activity for the FT synthesis. Therefore, it is expected on the basis of these facts mentioned above that a Co/SiO₂ catalyst can promote the ETP reaction without decomposition of propene which may be caused by the metathesis.

In this study, upon co-feeding a synthesis gas, namely a syngas (1:2 mixture of CO and H₂), with ethene, the formation rate of propene was increased 4-fold as much as that in the case feeding ethene alone.

2. EXPERIMENTAL

2.1. Preparation of Co/SiO₂ catalyst:

The catalyst was prepared by impregnating method. Aqueous solution of cobalt nitrate (II) hexahydrate (Co(NO₃)₂·6H₂O, GR, Kanto Chemical) was immersed into a silica gel (Silica gel 60, particle size: ca.0.2mm, surface area 410 m²/g, Merck) containing 10 wt.% of Co relative to the whole catalyst weight. The resulting material was aspirated to remove water at 55–60°C for several hours and it was further calcined at 520°C in air using an electric muffle furnace (Model FO300, Yamato Scientific) for 3 h.

2.2. Propene synthesis from ethene (ETP reaction):

The catalyst (1 mL) weighing 1.1g was set in the quartz made U-tube vessel as described in Fig. 1 and the temperature was increased to 500°C under streaming argon with 100 mL/min for 1 h. Then the hydrogen was fed into the catalyst bed at 500°C for 1 h to activate the catalyst before the reaction. The feeding gas was changed again to argon and the temperature was set at 240°C for 0.5 h. Finally 5 mL of n-hexadecane (n-C₁₆H₃₄, GR, Tokyo Kasei) as a solvent was injected to the catalyst bed. Bubbling with flowing argon was continued until the hydrogen could not be detected by a TCD gas chromatograph (Shimadzu GC14B) equipped with 3mm φ × 2m of column packed with Unibeads-C (GL Science) maintained at 80°C using argon as a carrier. The catalyst pretreatment stated above was performed at 0.02 MPa.

The ETP reaction was carried out by streaming ethene with a purity of 99.9% (Taiyo Nissan). Feeding rate of ethene was regulated by means of thermal mass flow controller (Model 5850E, Emerson) which was calibrated by a thin soap film gas meter. The feeding rate of ethene was set around 15.4 g(catalyst)·h·mol(C₂H₄)⁻¹. When a syngas was co-fed with ethene, 99.95% purity of compressed syngas containing 34.9% of carbon monoxide and 65.1% of hydrogen purchased from Taiyo Nissan was used. The reaction temperature and pressure was set at 240°C and 0.02 MPa, respectively.
Analysis of hydrogen, carbon monoxide, carbon dioxide, and methane was made by the TCD-GC and that of hydrocarbons was done by a FID-GC (Shimadzu GC8A) equipped with 3mm φ × 2m of column packed with VZ-10 (GL Science) maintained at 70oC.

2.3. Ethene metathesis reaction and the ETP reaction:
In order to evaluate simultaneously the olefin metathesis reaction which is inter-molecular exchanging reaction of terminal alkylidene and the ETP reaction, an equimolecular mixture of 12C2- and 13C2-ethene (6.7 kPa) was contacted on 500 mg of Co/SiO2 catalyst at 240oC. The 13C2-ethene with 99.5% purity of 13C (Isotec Inc.) was used. The catalyst was evacuated in the order of 10-2 Pa at 500 oC for 1 h then it was activated by reduction with 26.7 kPa of hydrogen at 500 oC for 1 h. Finally, it was evacuated again at 500oC for 1 h prior to these reactions. These reactions were performed in closed glass circulation system with a volume of 390 mL. The composition of propene (ETP) and that of 13C1-ethene (metathesis) were determined by a FID-GC and a quadrupole mass spectrometer (Pfeiffer Prisma, QMS-200), respectively.

3. RESULTS AND DISCUSSION
3.1. The ETP on Co/SiO2 catalyst:
When ethene was fed solely on Co/SiO2 catalyst at 240oC under 0.02 MPa with feeding rate of 15.4 g(catalyst) -h -mol(C2H4)-1, the conversion of ethene was 5.2%. The conversion was defined as Equation I.

\[
\text{Conv. of C}_2\text{H}_4 = \frac{\text{[C] in C}_2\text{H}_4 \text{(inlet)} - \text{[C] in C}_2\text{H}_4 \text{(outlet)}}{\text{[C] in C}_2\text{H}_4 \text{(inlet)}} \times 100
\]

Fig. 1. Continuous flow reaction system equipped with bubble column reactor.
PR: pressure regulator, MFC: thermal mass flow controller, M: mixer, CH: chucking valve, F: furnace, T: trap

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Fig. 2. The ETP reaction on Co/SiO2 catalyst at 240oC under 0.02 MPa with flowing ethene alone.
Catalyst: 1mL (1.1g), Loading amount of Co: 10 wt.%, Charding rate of ethene: 15.4 g(catalyst) -h -mol(C2H4)-1.

Fig. 3. The ETP reaction on Co/SiO2 catalyst with co-feeding ethene and syngas. The reaction conditions were the same as in Fig. 2. Expect co-feeding ethene and syngas. Volumetric proportion of syngas/ethene was 4.
Fig. 2 shows the synthesis rate in regard with hydrocarbons with 1-4 of carbon number. Hereinafter these were denoted as C₁, C₂, C₃ and C₄, respectively. C₂ was deleted from the figure because ethene was raw material for the reaction. As seen in the figure, the synthesis rate of C₁, C₃, and C₄ were trace, 0.82, and 0.32 mmol·h⁻¹, respectively. The C₃ and the C₄ were almost comprised of propene and 2-butene, respectively. Thus the formation of propene was dominantly formed on Co/SiO₂ catalyst.

Here one can suspect that the propene was formed through olefin metathesis route. In order to clarify whether olefin metathesis reaction is occurred on Co/SiO₂ or not in the ETP reaction, 1:1 mixture of ¹³C₂- and ¹²C₂-ethene was contacted on the catalyst in closed circulation system. Composition of propene was increased by elapsing time while that of ¹³C₁-ethene was not increased at all (Table I). Thus, it was conjectured that the catalyst could not be activated the metathesis reaction in the ETP reaction.

As mentioned above, traceable formation of C₁ (methane) was recognized in the reaction. After the reaction, the gas phase was once removed by flowing argon, and then feeding hydrogen with low flow rate such as 20 mL/min, whereupon slight amount of methane was detected. It could be explained, at least, from the result and the corroboration that slight amount of carbon species might be deposited from hydrocarbons which may react with hydrogen to produce methane. Analogous phenomenon is observed on Co/C and Co/Al₂O₃ catalysts, that is, carbon deposition from gas phase to cobalt surface is also suggested by using carbon monoxide at 210°C.

3.2. Enhancement of the ETP by co-feeding syngas:

The FT synthesis involves with chain propagation of methylidene (=CH₂) species as Equation II.

\[
2\text{H}_2 + \text{CO} \rightarrow \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O}. 
\]

It is widely accepted that the FT synthesis proceeds on Co, Fe, and Ru based catalysts. Particularly Co based catalyst is applied to the commercial FT plant using natural gas. If a part of methylidene species which generated via the FT route may participate in the ETP reaction, the enhancement of the propene formation will be anticipated on Co/SiO₂ catalyst.

Upon co-feeding ethene (15.4 g(catalyst)·h·mol(C₂H₄)-¹) and syngas with volumetric proportion of syngas/ethene=4 to Co/SiO₂ catalyst, the conversion of ethene showed 12.5%, and as a result, the conversion was increased 2.4 fold as much as that in the case flowing ethene alone. In addition, the conversion of carbon monoxide was 51.3% which was calculated by using the similar as the Equation I except using CO(inlet) and CO(outlet) instead of C₂H₄(inlet) and C₂H₄(outlet), respectively.

As shown in Fig.3, The synthesis rate of C₃ was 3.32 mmol·h⁻¹. This was 4 times larger relative to that in the case flowing ethene alone. It was inferred from the result that the propene formation was enhanced by the reaction with methylidene and ethene. Olefin/paraffin ratio in C₂, C₃, and C₄ was 3.0, 13.6, and 11.0, respectively. Thus the olefinicity was maintained in products despite the presence of hydrogen. It might be worthy interpretation for this that the hydrogenation of olefinic hydrocarbons was partially inhibited by carbon monoxide in the syngas.

Table I. Ethene metathesis reaction (inter-molecular =CH₂ exchanging of C₂H₄) and the ETP reaction on Co/SiO₂ catalyst at 240°C under 6.7 kPa.

<table>
<thead>
<tr>
<th>Reaction time/min</th>
<th>¹³C distribution in C₂H₄/%</th>
<th>Composition of C₂H₄/°°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>¹²C₀-C₂H₄</td>
<td>¹²C₁-C₂H₄</td>
</tr>
<tr>
<td>0</td>
<td>51.8</td>
<td>3.9</td>
</tr>
<tr>
<td>10</td>
<td>52.8</td>
<td>3.8</td>
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<tr>
<td>20</td>
<td>52.0</td>
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<tr>
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<tr>
<td>80</td>
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<td>3.7</td>
</tr>
<tr>
<td>160</td>
<td>52.8</td>
<td>3.8</td>
</tr>
</tbody>
</table>

*: by q-pole mass spectrometer with ionization voltage of 70eV
**: by FID-GC (minimum sampling interval was 30 min)


3.3. The FT synthesis on Co/SiO₂ catalyst:

In order to evaluate the formation rate of hydrocarbons by the FT synthesis on Co/SiO₂, the syngas was only introduced into the catalyst bed with same conditions except feeding no ethene. The conversion of carbon monoxide was 11.4%. As described in Fig. 4, synthesis rate of C₂ was 0.38 mmol h⁻¹. The conversion of carbon monoxide and the synthesis rate of C₃ were 0.22- and 0.03-fold as much as those stated in §3.2, respectively. Thus the suppressing of C₃ formation was more remarkable than in comparison with that of the conversion of carbon monoxide.

It was deduced that the propene synthesis proceeded via the reaction with methylidene and ethene. When syngas was only streaming, it was desired to form ethene through the dimerization of methylidene (2 =CH₂ → C₂H₄) following the methylidene formation by the hydrogenation of carbon monoxide as described in Equation II. It might be considered that the C₁ formation under feeding syngas alone was retarded because the reaction step was more complex compared to the case using gas mixture of syngas and ethene.

Here one can remind that the formation rate of C₁ using ethene alone was slower compared to the experiment feeding ethene and syngas (see §3.1 and §3.2). This result would be suggested that the formation of methylidene species from ethene was not occurred rapidly on that catalyst. In addition, the formation of C₁ was observed during the reaction using syngas in the presence and the absence of ethene, these were laid around 2.19 ~ 2.46 mmol·h⁻¹, i.e., these formation rates were approximately the analogous. It was considered that the formation of C₁ was caused by the hydrogenation of methylidene (=CH₂ + H₂ → CH₃) and that the methylidene formation would be instantly formed from syngas as in Equation II on Co/SiO₂ catalyst.

Other researchers suggest in supported ruthenium catalyst system which shows activity for the FT synthesis that the methylidene species readily reacts with ethene to form propene. If this was held in Co/SiO₂ catalyst system as well as the ruthenium catalyst, the C₁ formation was enhanced by rationally providing methylidene species through the hydrogenation of syngas (Equation II) and that species instantly reacted with ethene to form propene. In fact, the conversion of carbon monoxide streaming ethene and syngas was 51.3% whereas that of carbon monoxide using syngas alone was 11.4%. A part of the increase in regard with the conversion of carbon monoxide may reveal the consumption of =CH₂ by the reaction with ethene.

4. CONCLUSION

It was implied that the enhancement of the ETP reaction was induced by increasing the concentration of methylidene species via FT route which reacted readily with ethene. Finally, the ETP reaction was enhanced 4-fold as much as that in the case flowing ethene alone on Co/SiO₂ catalyst even in the low pressure like 0.02 MPa.

In order to understand the unique phenomenon, reaction path to obtain propene on Co/SiO₂ as in Fig. 5. It was deduced that the rate of chain propagation step via FT route, and the rate of methylidene supply from ethene was insufficient to yield propene rationally (→) while that the formation of =CH₂ from syngas was fast occurred on the catalyst.

If the =CH₂ supplied from syngas and ethene instantly reacted with ethene, the propene formation was effectively enhanced on Co/SiO₂ as in Fig. 5.

Author may expect, for instance, that this technique also has a potential to be applicable to fuel synthesis such as gas to liquid (GTL) process based on FT synthesis using associated gas including light olefins from gas fields.

References


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