HOMOLOGATION OF ETHYLENE WITHOUT METATHESIS ON SILICA SUPPORTED RUTHENIUM CATALYST

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

Received September 1, 2003
In revised form October 13, 2003
Accepted October 13, 2003

Abstract
A 1:1 mixture of $^{12}$C$_2$H$_4$ (H$_2$C=CH$_2$) and $^{13}$C$_2$H$_4$ (H$_2$C=$^{13}$CH$_2$) was contacted on Ru/SiO$_2$ at 200°C. Propylene (homologation) was observed without $^{12}$C$_2$H$_4$ formation (metathesis reaction). This might, at least, be corroborating evidence for discrimination of active sites in regard with the homologation and the metathesis.

Keywords: Homologation, chain elongation, Fischer-Tropsch synthesis, metathesis, disproportionation

INTRODUCTION

Ethylene homologation reaction ($3$C$_2$H$_4$ $\rightarrow$ $2$C$_3$H$_6$, denoted as homologation) proceeds on supported molybdenum and tungsten catalysts promoting olefin metathesis [1-3]. It is therefore accepted putatively that the homologation is analogous to the metathesis reaction via alkylidene and metallacyclic species. Basset et al. reported that the homologation of ethylene proceeds via bridged alkylidene and metallacyclic species on iron based Fischer-Tropsch (FT) catalyst [4]. Thus it can be understood that the homologation not only occurs on metathesis-active catalysts as Mo, W, etc., but also on a FT-active catalysts Fe [4] and Ru [5]. It is remarkable that Ru based catalysts may also have potential commercial application in FT synthesis similarly to Fe based-catalysts [6,7]. In addition, it was recently reported in organometallic chemistry that complexes including Ru show metathesis activities [8,9].
So far, some trials to discriminate the active sites of homologation and metathesis have been reported for supported molybdena catalyst systems [10-12]. For instance, in supported molybdena catalyst systems, the homologation does not proceed at all on MoO$_y$ (y=2.3-2.9) [12], whereas olefin metathesis proceeds instantly even on higher oxidation state molybdena species as MoO$_y$ (y=2.3-2.9) [11,12]. Thus, it seems that the metathesis-active catalyst is not always active for homologation but that the homologation-active catalyst also promotes the metathesis reaction. However, much less attention has been paid for demonstrations of the inverse phenomenon, *viz.*, homologation without the metathesis. If the inverse phenomenon can be observed on a heterogeneous catalyst, it will be corroborating evidence regarding the discrimination of active sites for these reactions.

In this paper, reduced Ru/SiO$_2$ and MoO$_y$/SiO$_2$ (x around 2) catalysts were subjected to metathesis and homologation reactions. The homologation and metathesis readily proceeded on MoO$_x$/SiO$_2$, whereas homologation was only recognized without metathesis on Ru/SiO$_2$. Thus, the inverse phenomenon (homologation without metathesis), was successfully confirmed and as a result, it is clearly indicated that active sites for homologation may require different factors relative to those for metathesis.

**EXPERIMENTAL**

The Ru/SiO$_2$ catalyst was prepared by the impregnation method. Silica (Kiesel Gel 60, Merck) having specific surface area of 430 m$^2$/g was used as a carrier. The silica was immersed into an aqueous solution of RuCl$_3$ hydrate (Mitsuwara Chemical Co., Ru assay 38 wt.%) to contain 2 wt.% ruthenium. The slurry was set in a rotary evaporator maintained at room temperature to remove water with aspiration, finally the resulting material was dried in an oven maintained at 50°C for 12 h. The catalyst (500 mg) was activated by reduction with hydrogen (20 kPa) at 500°C for 2 h prior to the reaction. After pumping off hydrogen, homologation and metathesis were simultaneously evaluated by using a 1:1 mixture of $^{13}$C$_2$C$_2$H$_4$ and $^{12}$C$_2$C$_2$H$_4$ at ca. 2.67 kPa at 200°C. The MoO$_y$/SiO$_2$ catalyst was also prepared by impregnation method using an aqueous solution of (NH$_4$)$_6$MoO$_{24}$ (Wako Chemical Co.) to contain 6.7 wt.% of molybdenum. The preparation procedure was the same as for the Ru/SiO$_2$ catalyst except for using (NH$_4$)$_6$MoO$_{24}$. The x value of MoO$_x$ was determined by consumption of hydrogen during reducing the catalyst. Catalyst activation and reaction were carried out a conventional glass closed circulation system with a volume of 420 mL. Products were analyzed by gas chromatography and $^{13}$C distribution in C$_2$H$_4$ was determined by mass spectrometry.
RESULTS AND DISCUSSION

Figure 1 shows C₃ formation (homologation) and ¹³C₁-C₂H₄ formation (metathesis, $^{12}$C₂-C₂H₄ + $^{13}$C₂-C₂H₄ ⇋ 2 $^{13}$C₁-C₂H₄) on the reduced MoOₓ/SiO₂ (x was around 2) in the absence and presence of H₂. When 2.67 kPa of a 1:1 mixture of $^{12}$C₂-C₂H₄ and $^{13}$C₂-C₂H₄ was introduced on the reduced MoOₓ/SiO₂, $^{13}$C₁-C₂H₄ (the metathesis) was rapidly increased and finally the composition was reached around 47-48% which was almost the analogous to equilibrated value (50%) as seen in the figure. In contrast to metathesis, propylene formation (homologation) was recognized after 90 min. When 666.7 Pa of H₂ was added to the reaction, the composition of C₃H₆ and C₃H₈ was increased significantly and reached 2.5% after 330 min. Upon adding hydrogen, the formation of C₂H₆ and that of C₃H₆ gradually increased on the catalyst, which might be caused by hydrogenation via the following scheme:

```
Hydrogenation    C²H₅
                ↑
C₂H₄             C₃H₈
                 ↑
                Homologation
                → C₃H₆

Hydrogenation
```
Actually, C₂H₆ and C₃H₈ shared around 10% in gas phase at 330 min. In addition, the C₄ fraction was not detected under our reaction conditions, hence, it is concluded that the C₃ fraction was produced via the homologation path without inverse propylene metathesis such as C₂H₄ + C₃H₈ → 2 C₃H₆.

It is therefore confirmed that reduced MoOₓ/SiO₂ catalyzed both metathesis and homologation and that hydrogen addition was effective to promote homologation reaction.

In order to elucidate homologation and the metathesis on Ru/SiO₂, the catalyst was subjected to these two reactions in the same conditions using MoOₓ/SiO₂. Feeding the mixture of ¹³C labeled ethylene (proportion of ¹²C₂-C₂H₄ and ¹³C₂-C₂H₄ was unity, pressure 2.67 kPa) to the Ru/SiO₂ catalyst without H₂, propylene due to homologation was detected in the initial stage of the reaction and its composition was ca. 1% at 90 min as is shown in Fig. 2.

![Fig. 2. Ethylene homologation and metathesis on Ru/SiO₂ catalyst.](image)

Reaction conditions: same as in Fig. 1

When 666.7 Pa of H₂ was added in the middle course of the reaction, the formation of C₃ hydrocarbons (C₃H₆ and C₃H₈) was further increased and the C₃ fraction was ca. 1.5% at 120 min. This confirms that ethylene homologation proceeded on the Ru/SiO₂ catalyst. However, in the Ru/SiO₂ catalyst system, the increase of C₃ was rapidly saturated relative to the case using MoOₓ/SiO₂. It is deduced that retardation of homologation might be caused by diminishing
hydrogen, which was induced by the hydrogenation of olefins. In practice, the paraffins \((C_{2}H_{6}, C_{3}H_{8})\) formation at 60 min after adding \(H_{2}\) was increased 1.7 fold as much as that in the MoO\(_{3}/\)SiO\(_{2}\) system.

In contrast to homologation, metathesis did not proceed at all on Ru/SiO\(_{2}\). Here, one can suspect that the \(^{13}\)C\(_{1}-C_{2}H_{4}\) in the initial stage was involved in the metathesis, however, the ca. 10 % of \(^{13}\)C\(_{1}-C_{2}H_{4}\) was already included in the \(^{13}\)C labeled reagent with \(^{13}\)C purity of ca. 90 %. It might be conjectured from the results that homologation proceeded individually without metathesis on the Ru/SiO\(_{2}\).

In organometallic chemistry, Ru complexes show metathesis activity which is improved by maintaining high valency of Ru, such as Ru(IV), in the metallacyclic intermediates [9,13]. If this condition can be met in our experimented system, it could be considered that homologation was promoted while the metathesis was suppressed on lower valent ruthenium species.

As a conclusion, homologation without metathesis was achieved on a Ru/SiO\(_{2}\) catalyst. It is clearly indicated with taking account in the results reported on supported molybdena catalysts [10-12] that requirements of the active sites for homologation differed from those for metathesis. This result may shed light on the possibility to prepare a catalyst for the selective homologation reaction. From the industrial viewpoint, selective oligomerization related to homologation is important for converting light olefins to fractions of LPG (C\(_{3}-C_{4}\)) or liquid fuels (C\(_{5+}\)) in the commercial FT process [14].

Acknowledgement. Part of this work was carried out at Shinshu University when the author was faculty staff of the university.

REFERENCES