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Propane Metathesis by a Tandem Catalytic System: Dehydrogenation and Hydrogenation over $PtSn/Al_2O_3$, and Metathesis over Re_2O_7/Al_2O_3

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Metathesis of propane into *n*-butane and ethane using a tandem catalytic system consisting of two catalysts ($PtSn/Al_2O_3$ for dehydrogenation of alkane and hydrogenation of alkene, and Re_2O_7/Al_2O_3 for alkene metathesis) has been investigated. When the temperatures of two catalyst-beds are controlled independently, this system shows high conversion and is selective for the formation of *n*-butane.

Alkane metathesis (eq 1) for the transformation of lower alkanes into higher homologues has attracted attention, and is still a challenge in chemistry.

$$2C_nH_{2n+2} \rightleftharpoons C_{2(n-1)}H_{4(n-1)+2} + C_2H_6 \qquad (1)$$

Petroleum contains alkanes as major components. In the move toward various carbon sources including coal, natural gas, and biomass to replace petroleum products due to oil production decline, the Fischer–Tropsch (F–T) process (reductive oligomerization of CO and H_2) to produce synthetic fuel appears to become increasingly important. Production of diesel fuel by F–T process is attractive since major products consist of higher alkanes with a quite low sulfur content (<1 ppm). However, F–T process yields an alkane mixture with no molecular weight control. Moreover, a variety of refinery and petrochemical streams and biomass conversions give a large amount of light alkanes. Unfortunately, there is no practical process to convert a mixture of light alkanes into higher homologues. Thus, the development of an effective catalytic system for alkane metathesis is promising for converting light alkanes, and provides a great impact to industrial chemistry.

There have been many discussions on the reaction mechanism of alkane metathesis. It is commonly believed that alkane metathesis proceeds in three steps; alkane dehydrogenated to alkene and then the resulting alkene is transformed to higher alkene by metathesis. Finally, the formed higher alkene is hydrogenated to corresponding alkane.[1–8] Based on this mechanism, several efforts have been devoted to combine the functions of catalysts (dehydrogenation/hydrogenation and metathesis) in alkane metathesis. Burnett and Hughes reported the first catalytic alkane metathesis, the so-called Chevron process in the 1970s which was carried out in a continuous flow system.[1] But this system requires extremely high pressure of alkanes to obtain enough concentration of intermediate olefins. Recently, Goldman et al. reported a homogeneous catalytic system of tandem alkane metathesis using Ir-based pincer complexes for dehydrogenation and a Schrock-type Mo catalyst for olefin metathesis.[2,3] Although their system exhibits good performance for liquid alkanes, the homogeneous system is essentially inadaptable for light gaseous alkanes. On the other hand, the heterogeneous alkane metathesis by single-site catalyst such as alumina-supported tungsten hydride ($W(H)_3/Al_2O_3$) has also been reported by Basset and his co-workers.[4–8] They reported that this single-site catalyst operates via the metal centers with alkanes to give metal–carbene complex (α-H elimination) as well as free olefins (β-H elimination and β-alkyl transfer). This catalyst works under moderate conditions, however, product yields are low and delicate treatments are required for the catalyst preparation.

In this study, we investigated a tandem alkane metathesis by using two kinds of heterogeneous catalysts that can be prepared easily. $PtSn/Al_2O_3$ and Re_2O_7/Al_2O_3 have been employed as a dehydrogenation/hydrogenation catalyst and a metathesis one in this system. $PtSn/Al_2O_3$ is well known as a typical dehydrogenation catalyst and to suppress coking and cracking.[9–11] Re_2O_7/Al_2O_3 catalyst shows high catalytic activity for olefin metathesis even at ambient temperature.[12–14] These catalysts were easily prepared by a conventional impregnation method from γ-Al_2O_3 (JRC-ALO-4), $[Pt(NH_3)_4](NO_3)_2$, $SnCl_2{\cdot}2H_2O$, and NH_4ReO_4.[15] The loading amount of Pt was 0.6 or 1.0 wt %, with 0.6 of Pt/Sn molar ratio. The loading amount of Re_2O_7 was 18 wt % which showed the highest activity in olefin metathesis.[12,14] The alkane metathesis was carried out in a closed circulation system with twin reactors as shown in Figure 1a. The twin reactors were placed in two furnaces, therefore, the temperature of catalyst-beds can be controlled independently. $PtSn/Al_2O_3$ catalyst was mounted in the first reactor and Re_2O_7/Al_2O_3 in the second. Before the reaction, $PtSn/Al_2O_3$ was reduced at 773 K for 2 h in 6.7 kPa of H_2 and Re_2O_7/Al_2O_3 was oxidized at 673 K for 1 h

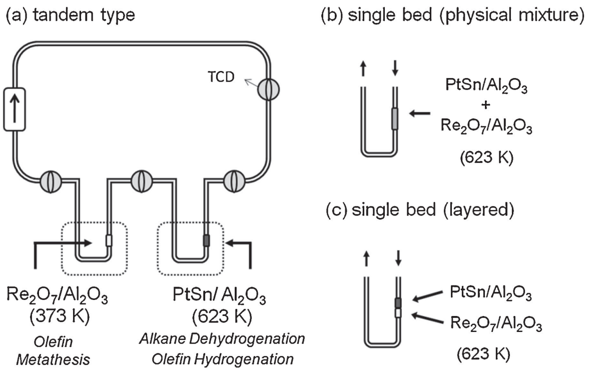

Figure 1. The outline of the catalytic system of (a) tandem type alkane metathesis and single bed type; the two catalysts were (b) physically mixed or (c) layered.

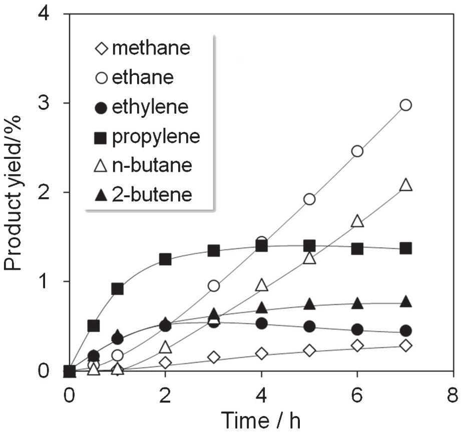

Figure 2. Time course of product yields of propane metathesis catalyzed by tandem system of 0.6 wt% $PtSn/Al_2O_3$ (Pt/Sn = 0.6) and 18 wt% Re_2O_7/Al_2O_3. $PtSn/Al_2O_3$; 623 K, Re_2O_7/Al_2O_3; 373 K.

in 6.7 kPa of O_2, respectively. The platinum dispersion of the pretreated $PtSn/Al_2O_3$ catalyst was determined to be 19% by CO pulse chemisorption.[15] The reactant, 13.3 kPa (1070 µmol) of propane was introduced ($C_3H_8/Pt = 210$, $C_3H_8/Re = 14.4$). The reaction temperature was kept at 623 K for $PtSn/Al_2O_3$ and 373 K for Re_2O_7/Al_2O_3, respectively. The products were analyzed by online TCD gas chromatograph. The time course of product yields of propane metathesis is shown in Figure 2. At the initial stage, C2, C3, and C4 olefins were formed in the ratio of 1:2:1, and then the yields plateaued. Hydrogen was also evolved in nearly equimolar amount to the olefins. After that, the yields of ethane (C2) and *n*-butane (C4) linearly increased as the reaction time increased, suggesting that propylene metathesis and subsequent hydrogenation proceeded. The ratio of *cis*/*trans*-2-butene was about 1/3 at any time. These changes in the product distribution suggest that a set of following reactions proceed sequentially (eqs 2–5). The reason why the formation of the olefins plateaus may be promotion of subsequent hydrogenation due to accumulation of hydrogen.

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2 \tag{2}$$

$$2C_3H_6 \rightleftharpoons C_2H_4 + 2\text{-}C_4H_8 \tag{3}$$

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6 \tag{4}$$

$$2\text{-}C_4H_8 + H_2 \rightleftharpoons n\text{-}C_4H_{10} \tag{5}$$

The yield of ethane was larger than that of *n*-butane. In contrast, the yield of ethylene became smaller than that of 2-butene after 3 h of reaction where alkanes were dominant. These may be because hydrogenation of ethylene is kinetically more favorable than that of 2-butene due to steric hindrance. Figure 3 shows the product distributions of propane metathesis over tandem- and single-bed catalytic systems after 7 h of reaction. Two kinds of single-bed systems in which the two catalysts were physically mixed or layered (Figures 1b and 1c) were compared with the tandem catalytic system. The reaction temperature of the single bed was kept at 623 K in each case. Although dehydrogenation of propane to propylene proceeded, no product of propylene metathesis (2-butene and ethylene) was obtained by using two kinds of single-bed systems. A trace of methane and ethane was obtained, suggesting that undesired cracking of propane occurred. On the other hand, the tandem system gave *n*-butane and ethane as main products. It appears that controlling the temperature of each catalyst bed independently is necessary in order to undergo propylene metathesis. The yields of ethane and *n*-butane increased as the reaction time increased as shown in Figure 4. The selectivity to *n*-butane in C4 products (C4/(C4 + C4//)), total yield of C4 and C5 alkanes and propane conversion reached 92%, 7.5%, and 21%, respectively after 120 h. Moreover, turnover number (mol of converted C_3H_8 per mol of surface Pt atom estimated by CO pulse chemisorption)[15] was up to 233 after 120 h, which is much higher than that of $W(H)_3/SiO_2–Al_2O_3$ catalyst reported by Basset et al. (120 after 120 h).[7] Although the yield of 1-butene was negligible, a small amount of pentane (0.3%) was observed. In addition, the tandem system gave no branched alkane such as isobutane and isopentane.

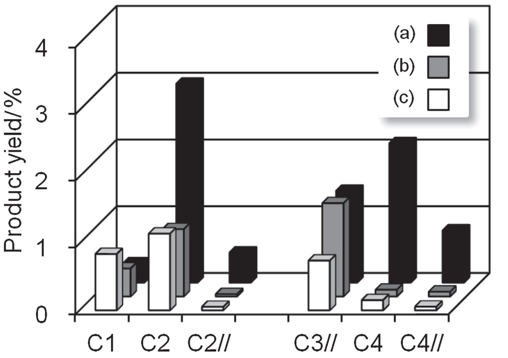

Figure 3. Product distribution after 7 h of propane metathesis catalyzed by 0.6 wt% $PtSn/Al_2O_3$ (Pt/Sn = 0.6) and 18 wt% Re_2O_7/Al_2O_3; tandem type (a, $PtSn/Al_2O_3$; 623 K, Re_2O_7/Al_2O_3; 373 K), physically mixed (b, 623 K) and layered (c, 623 K). C2, C3, and C4 olefins are abbreviated to C2//, C3//, and C4//, respectively.

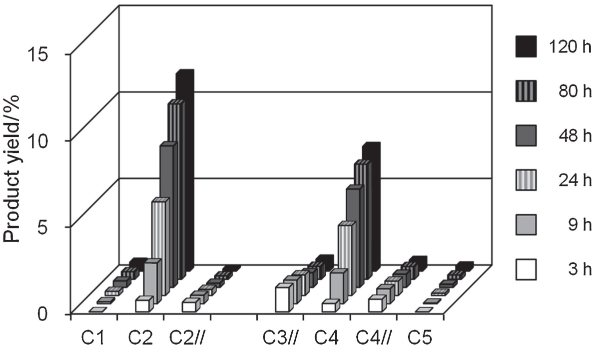

Figure 4. Time course of product distribution of propane metathesis catalyzed by 1.0 wt% $PtSn/Al_2O_3$ (Pt/Sn = 0.6) and 18 wt% Re_2O_7/Al_2O_3. $PtSn/Al_2O_3$; 623 K, Re_2O_7/Al_2O_3; 373 K. C2, C3, and C4 olefins are abbreviated to C2//, C3//, and C4//, respectively.

In conclusion, the results show the great effectiveness of the tandem catalytic system for alkane metathesis. Although the optimization of some conditions such as reaction scale, reaction temperature, catalyst amount, and Pt/Sn ratio are yet to be investigated, the tandem system has very flexible reaction conditions and many possible combinations of dehydrogenation/hydrogenation and metathesis catalysts, depending on the nature of alkanes. It was found that controlling temperature of the two catalyst-beds independently is important for alkane metathesis. These findings have opened up an opportunity for tandem alkane metathesis in a continuous flow system.

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