[Regular Paper]

Effect of Iterative Use of Methylcyclohexane as a Hydrogen Carrier on Catalytic Activity and By-product Formation

Xieli CUI^{†1)*}, Mika ISHII^{†1)}, Taku TSUJIMURA^{†1)}, Takaaki TANIGUCHI^{†2)},
Yasushi HASHIMOTO^{†2)}, and Tetsuya NANBA^{†1)*}

^{†1)} Renewable Energy Research Center, National Institute of Advanced Industrial Science and Technology (AIST),
2-2-9 Machiikedai, Koriyama, Fukushima 963-0298, JAPAN

^{†2)} Central Technical Research Laboratory, JXTG Nippon Oil & Energy Corp., 8 Chidori-cho, Naka-ku, Yokohama 231-0815, JAPAN

(Received September 12, 2018)

Methylcyclohexane (MCH) is a candidate liquid organic hydrogen carrier for the storage of renewable energy. The by-products were examined in dehydrogenation and hydrogenation of the MCH/toluene (TOL) pair that forms an energy storage and release system. Pt catalyst was used for the dehydrogenation of MCH, and Ni catalysts were used for the hydrogenation of TOL, and 10 cycles of dehydrogenation/hydrogenation were conducted. Conversion of TOL to MCH greater than 97 % across all cycles, and conversion of MCH to TOL decreased from 90 to 84 %, with increasing cycle number. The original MCH feed contained 0.6 % impurities, and the concentration of by-products ranged from 0.7–0.9 %. More than 70 by-products were identified in the liquid product, and were categorized as the products of six types of side reactions: demethylation, ring-opening, isomerization to form 5- or 6-membered ring compounds, dimerization, and polycyclic compound formation. Demethylation compounds showed remarkable accumulation after 10 cycles.

Keywords

Hydrogen carrier, Methylcyclohexane, Toluene, By-product, Iterative use, Catalytic activity

1. Introduction

Renewable sources of energy are important alternatives to fossil fuels because they produce no emissions. However, their power densities are much lower than those of fossil fuels. Integrated renewable power-generation systems, such as photovoltaic modules and wind turbines, are a promising approach to achieving high output, but effective methods for storing renewable energy at high density are needed. Hydrogen energy storage systems are a promising approach in which renewable energy is used to power electrolysis to produce hydrogen that can then be stored indefinitely. Hydrogen is a clean fuel which stores pure, high-density energy. Compression and liquefaction of hydrogen are important techniques required for clean energy storage.

Recently, organic hydrides derived from petroleum, such as methylcyclohexane (MCH), cyclohexane, and decalin, have been proposed as candidate hydrogen carriers for the transportation and storage of hydrogen^{1)–3)}. MCH is a liquid at ambient temperature, with ignition point of 309 °C, so is relatively easy to handle under

ambient conditions. In addition, MCH allows high hydrogen density storage, as almost 500 NL of H₂ can be stored in 1 NL of liquid MCH.

Energy storage systems using MCH as the hydrogen carrier are based on two reactions in which MCH is dehydrogenated to toluene (TOL), and the toluene product is then hydrogenated back to MCH. The costs associated with such systems are reduced by reusing the products of both reactions in future MCH dehydrogenation/TOL hydrogenation cycles (**Fig. 1**)^{4)–6)}. Several highly active catalysts for these reactions have been proposed^{7)–10)}. Dehydrogenation of MCH over Pt catalysts is a highly selective reaction that produces TOL, H₂, and few by-products^{6),10)}, which include benzene,

TOL, toluene.

Fig. 1 Iterative Use of Methylcyclohexane (MCH) as a Hydrogen Carrier

DOI: doi.org/10.1627/jpi.62.67

* To whom correspondence should be addressed.

* E-mail: sai-xieli@aist.go.jp, tty-namba@aist.go.jp

methane, xylenes, etc.

Generally, in catalytic chemical processes, feed gases are passed through a catalyst bed, and the desired products and small amounts of by-products are formed. However, iteration of a catalytic chemical process causes accumulation of the by-products in the liquid product, which can strongly influence the reactions in future cycles. Therefore, these by-products must be removed by appropriate processes (*e.g.*, distillation). However, by-product accumulation in iterative MCH-based energy storage systems is not understood¹¹.

The present study investigated the behavior of by-products formation during iterative use of MCH dehydrogenation/TOL hydrogenation in an integral catalytic reactor.

2. Experimental

MCH (purity, >99.0 %) was purchased from Sankyo Chemical Co., Ltd., Japan. Pt catalyst (JXTG Nippon Oil & Energy Corp., JX) and Ni catalyst (BASF, Ni5256) were used for the MCH dehydrogenation and TOL hydrogenation reactions, respectively. Catalytic activity tests used a fixed-bed flow reactor system (Fig. 2). Dehydrogenation of MCH used a single tubular reactor (reactor volume, 200 mL; reactor bed length, 570 mm). Hydrogenation reactions used two identical tubular reactors in series (reactor volume, 100 mL; reactor bed length, 500 mm). The hydrogenation and dehydrogenation reaction systems were based on double-walled reactor tube, and cooled heat-

ing fluid (Julabo Japan Co., Ltd.) was circulated to remove heat from the reactor. H₂ (purity, >99.99 %; dried) was supplied to the reactor from a water electrolyzer (GS Yuasa Corp.). The product of the first MCH dehydrogenation was used as the feed for the subsequent TOL hydrogenation reaction, and then the product of that reaction was used as the feed for the next cycle, so that the MCH was dehydrogenated a total of 10 times. The products of the two reactions were analyzed by on-line gas chromatograph equipped with a flame-ionization detector (GC-FID). Liquid products were collected after cooling of the effluent gas and then analyzed by GC-FID using a DB-1 column (40 m × 100 μm I.D., 0.2 μm film thickness) and ramping rate of column temperature, 10 °C/min from 60 to 325 °C.

Catalytic activity was expressed as MCH and TOL conversions calculated from Eqs. (1) and (2). Carbon ratio (C%) proportional to the number of carbon atoms in a product was calculated from the area of the identified peak and C% converted to mol% by Eq. (3).

$$\text{MCH conversion [\%]} = \frac{\text{TOL concentration in product [ppm]}}{(\text{MCH} + \text{TOL}) \text{ concentration in product [ppm]}} \times 100 \quad (1)$$

$$\text{TOL conversion [\%]} = \frac{\text{MCH concentration in product [ppm]}}{(\text{MCH} + \text{TOL}) \text{ concentration in product [ppm]}} \times 100 \quad (2)$$

GC-FID, gas chromatograph equipped with flame-ionization detector. MFC, mass flow controller.

Fig. 2 Process Flow Diagram of the Fixed-bed Flow Reactor System Used to Conduct the Methylcyclohexane (MCH) Dehydrogenation and Toluene (TOL) Hydrogenation Reactions

MCH, methylcyclohexane; TOL, toluene.

Fig. 3 Representative Temperature Distributions after 10 Cycles of MCH Dehydrogenation (reactor 1) and TOL Hydrogenation (reactors 2-1 and 2-2)

$$\text{Concentration of by-product [mol\%]} = \frac{\text{Identified by-product concentration in product [ppm]}}{\sum (\text{Identified product concentration [ppm]} / \text{carbon number})} \times 100 \quad (3)$$

3. Results and Discussion

3.1. Catalytic Activities and By-product Formation

MCH dehydrogenation is an endothermic reaction, whereas TOL hydrogenation is an exothermic reaction; the overall enthalpy change for the two reactions is 205 kJ/mol. The reaction temperature varied along the length of the catalyst beds; representative temperature distributions after 10 cycles of MCH dehydrogenation and TOL hydrogenation reactions are shown in **Fig. 3**. Marked decrease from the set temperature of the heating fluid was observed at 50 mm from the reactor inlet in reactor 1, which we attributed to endothermic MCH dehydrogenation, after which the temperature began to increase. The highest temperature, equal to the set temperature, was recorded at the reactor outlet. Increases from the set temperature were observed at 200 mm and 50 mm, respectively, from the reactor inlets in reactors 2-1 and 2-2, which we attributed to exothermic TOL hydrogenation. These results suggest that MCH dehydrogenation occurred only in reactor 1, whereas TOL hydrogenation occurred in both reactors 2-1 and 2-2. The percentage conversions of MCH to TOL and of TOL to MCH for each of the 10 cycles are shown in **Fig. 4**. The amount of TOL converted was greater than 97 % for each cycle. In contrast, the

Fig. 4 Conversion of Methylcyclohexane (MCH) and Toluene (TOL) at Each Cycle, as Determined by the GC-FID

amount of MCH converted in the first cycle exceeded 90 % but had decreased to 84 % by the final cycle.

The total concentrations of by-products in the liquid product and the concentration of CH₄ produced after each dehydrogenation and hydrogenation are shown in **Fig. 5**. CH₄ concentrations were determined by on-line GC-FID after condensation of the effluent gas. Impurities accounted for approximately 0.6 % of the original MCH feed. By-products accounted for approximately 0.8 % of the liquid product after the first dehydrogenation. The percentage of by-products in the liquid product then gradually increased with increasing cycle number until the sixth cycle (0.9 %), and then remained roughly constant. High concentrations of CH₄ were produced by the first dehydrogenation and

Fig. 5 Concentrations of Total By-products in the Liquid Product and Methane Concentration in the Effluent Gas, as Determined by the GC-FID

Fig. 6 Change in By-product Composition in the Liquid Product by Carbon Number

hydrogenation, but decreased by approximately 32 % and 70 % at the second dehydrogenation and hydrogenation, respectively; CH₄ concentration then fluctuated between consistent highs after dehydrogenation and consistent lows after hydrogenation. **Figure 5** suggests that the concentration of CH₄ decreased with increasing cycle number.

3.2. Change in By-product Composition

Detailed analysis of the by-products in the liquid product was performed after each dehydrogenation and hydrogenation reaction. More than 70 by-products were detected, which were categorized by carbon number (**Fig. 6**). The major impurity in the original MCH feed was C7 compounds followed by C6 and C8 compounds; few C9-C12 and C13+ compounds were present. With increasing cycle number, the concentration of C7 compounds decreased and that of C6 compounds increased; the concentration of C8 and C13+ compounds markedly increased, and that of C9-C12 compounds slightly increased.

The greatest increase in by-products was found with the C6 compounds, so these by-products were further characterized as a mixture of benzene, cyclohexane,

Fig. 7 Change in C6 By-product Concentration in the Liquid Product

Fig. 8 Classification of By-products by Side Reactions

and paraffins (**Fig. 7**). The concentration of benzene markedly increased with each dehydrogenation process and then decreased to almost zero with each hydrogenation process. Similarly, the concentration of cyclohexane markedly increased with each hydrogenation process and then decreased, but not totally, with each dehydrogenation process. The total benzene and cyclohexane concentration at each dehydrogenation step was larger than the concentration of cyclohexane in the previous hydrogenation step, suggesting that accumulation of cyclohexane and benzene was a result of MCH dehydrogenation. Benzene can be converted into cyclohexane, so the cyclohexane-benzene pair likely acted as a secondary hydrogen carrier in addition to the MCH-TOL pair.

The detected by-products were also categorized by the type of side reaction they were produced by: demethylation, ring-opening, isomerization to form 5- or 6-membered ring compounds, dimerization, or polycyclic compound formation (**Fig. 8**). Note that MCH, TOL, benzene, and cyclohexane were excluded from

Fig. 9 Change in By-product Composition in the Liquid Product Formed by Side Reactions

the 6-membered ring compound category. **Figure 9** shows the changes in the by-products found in the liquid product with increasing cycle number. The concentration of by-products produced by demethylation increased with increasing cycle number until the fifth dehydrogenation process, then became stable. The concentration of by-products produced by ring-opening remained constant with increasing cycle number. The concentration of by-products produced by dimerization increased gradually. The concentration of by-products produced by isomerization into 6-membered ring compounds increased with dehydrogenation and decreased with hydrogenation. Conversely, the concentration of by-products produced by isomerization into 5-membered ring compounds decreased with dehydrogenation and increased with hydrogenation. The concentration of fluorenes, which are typical products of multi-cyclization reactions, was very low across all cycles. These results show that the major by-products were demethylation compounds. Additionally, carbonaceous depositions were anticipated to be formed on the surfaces of both hydrogenation and dehydrogenation catalysts. Such carbonaceous depositions will be investigated in the future.

In addition to the cyclohexane–benzene and MCH–TOL compound pairs, several other pairs of by-products were believed to have hydrogen storage/release functions. For example, the xylene/dimethylcyclohexane pair has a potential storage/release function (**Fig. 10**). However, the concentration of xylenes in the ninth dehydrogenation cycle was 0.080 %, and the concentration of dimethylcyclohexane in the ninth hydrogenation cycle was 0.025 %. Therefore, the xylenes formed other compounds in addition to dimethylcyclohexane. Consequently, we focused on the formations of 6- and 5-membered ring compounds. As shown in **Fig. 9**, the concentration of 6-membered ring compounds increased in the dehydrogenation cycle. The formation of 6-membered ring compounds may involve reaction of methyl radicals formed from demethylation. The

Fig. 10 Changes in the Concentration of 5- and 6-Membered Ring By-products in the Liquid Product by Molecular Structure

concentration of 5-membered ring compounds increased in the hydrogenation cycle. The formation of 5-membered ring compounds probably occurred through isomerization of 6-membered ring compounds^{12)–15)}. Detailed analysis of the 5-membered-ring compounds revealed that 1-ethyl-2-methylcyclopentane was the most abundant compound. The concentration of 1-ethyl-2-methylcyclopentane increased with hydrogenation and fell to almost zero with dehydrogenation. In contrast, the concentrations of other 5-membered ring compounds in the ninth dehydrogenation and hydrogenation cycles were 0.033 % and 0.039 %, respectively. Therefore, the change in the concentration of 5-membered ring compounds was due to the formation and consumption of 1-ethyl-2-methylcyclopentane.

To confirm that 1-ethyl-2-methylcyclopentane was formed from the 6-membered ring by-products, hydrogenation of xylenes was investigated. 1-Ethyl-2-methylcyclopentane possesses eight carbons, so that xylenes and ethylbenzene are the candidate precursors for 1-ethyl-2-methylcyclopentane formation. The concentration of xylenes was greater than that of ethylbenzene, so xylene formation was examined in this model experiment. *p*-Xylene (*p*-XL, FUJIFILM Wako Pure Chemical Corp.) and *m*-xylene (*m*-XL, FUJIFILM Wako Pure Chemical Corp.), both obtained at more than 99.8 % purity from GC-FID were hydrogenated and conversions and by-products are shown in **Figs. 11(a)** and **11(b)**, respectively. Conversions of 99 % and 95 % were obtained for *p*-XL and *m*-XL, respectively. These results suggest differences in reactivity that depended on the position of the methyl group, and that *p*-XL was more easily hydrogenated. **Figure 11(a)** shows the formation of 1,3- and 1,4-dimethylcyclohexane in both reactions. Interestingly, the dominant product of *p*-XL hydrogenation was 1,3-dimethylcyclohexane, even though 1,4-dimethylcyclohexane has the same molecular configuration as *p*-XL. Xylene hydrogenation produced various by-

Fig. 11 Products (a) and By-products (b) of *m*- and *p*-Xylene Hydrogenation

products, including compounds produced by ring-opening, demethylation, isomerization to form 5- or 6-membered ring compounds, dimerization, and polycyclic compound formation, as well as hydrogenation of toluene. In the case of *p*-XL, most by-products (2.2 %) were produced by ring-opening. Only 0.01 % and 0.07 % of the products were 5- and 6-membered ring compounds, respectively. The major 5-membered ring by-product was 1-ethyl-2-methylcyclopentane. In the case of *m*-XL hydrogenation, fewer by-products were detected compared with *p*-XL hydrogenation, although more demethylation by-products were found. In addition, fewer by-products were produced by ring-opening, 5-membered ring formation, or polycyclic compound formation. These results suggest that 1-ethyl-2-methylcyclopentane can be produced as a minor by-product of hydrogenation of *p*-XL. Therefore, the observed 1-ethyl-2-methylcyclopentane formation during the hydrogenation cycle is unlikely to originate from *p*-XL hydrogenation. Therefore, 1-ethyl-2-methylcyclopentane is probably formed from other 6-membered-ring compounds, not only *p*-XL.

4. Conclusion

Highly efficient evolution of hydrogen was achieved from iterative use of methylcyclohexane as a liquid organic hydrogen carrier in an integral catalytic reactor system with accumulation of about 0.3 % of by-products after 10 cycles. Demethylation was the most important side reaction, but accumulation of by-products in MCH/TOL did not cause effective catalyst deactivation. Benzene and cyclohexane derived from demethylation were the main by-products of the MCH dehydrogenation and TOL hydrogenation reaction, respectively. Benzene was accumulated in MCH dehydrogenation, and then almost totally converted in TOL hydrogenation, suggesting that demethylation products mainly accumulated in MCH dehydrogenation. The amount of 6-membered ring by-products increased during dehydrogenation and decreased in hydrogenation. Conversely, the amount of 5-membered ring by-products decreased during dehydrogenation and increased in hydrogenation. *p*-Xylene may be the precursor of 1-ethyl-2-methylcyclopentane.

Acknowledgment

This study was conducted with the support of the Japan Petroleum Energy Center as a technological development project funded in part by the Ministry of Economy, Trade, and Industry of Japan.

References

- 1) Kariya, N., Fukuoka, A., Utagawa, T., Sakuramoto, M., Goto, Y., Ichikawa, M., *Appl. Catal. A: Gen.*, **247**, 247 (2003).
- 2) Biniwale, R. B., Kariya, N., Yamashiro, H., Ichikawa, M., *J. Phys. Chem. B*, **110**, 3189 (2006).
- 3) Biniwale, R. B., Rayalua, S., Devotaa, S., Ichikawa, M., *Int. J. Hydrogen Energy*, **33**, 360 (2008).
- 4) Alhumaidan, F., Cresswell, D., Garforth, A., *Energy & Fuels*, **25**, 4217 (2011).
- 5) Schere, G. W. H., Newson, E., Wokaun, A., *Int. J. Hydrogen Energy*, **24**, 1157 (1999).
- 6) Newson, E., Haueter, T., Hottinger, P., Vonroth, F., Scherer, G. W. H., Schucan, T. H., *Int. J. Hydrogen Energy*, **23**, 10 (1998).
- 7) Gonda, M., Ohshima, M., Kurokawa, H., Miura, H., *Int. J. Hydrogen Energy*, **39**, 16339 (2014).
- 8) Al-ShaikhAki, A., Jedidi, A., Anjum, H. D., Cavallo, L., Takanabe, K., *ACS Catal.*, **7**, 1592 (2017).
- 9) Yolcular, S., Olgun, O., *Catalysis Today*, **138**, 198 (2008).
- 10) Nagatake, S., Higo, T., Ogo, S., Sugiura, Y., Watanabe, R., Fukuhara, C., Sekine, Y., *Catal. Lett.*, **146**, 1 (2016).
- 11) Cui, X., Ishii, M., Takano, K., Nanba, T., Tsujimura, T., Taniguchi, T., 252nd ACS National Meeting, Philadelphia, ENFL, **232**, (2016).
- 12) Usman, M., Cresswell, D., Garforth, A., *ISRN Chemical Engineering*, Article ID 818953, 7 (2012).
- 13) Alhumaidan, F., Tsakiris, D., Cresswell, D., Garforth, A., *Int. J. Hydrogen Energy*, **38**, 14010 (2013).
- 14) Rallan, C., Ph. D. thesis, The University of Manchester, Manchester, UK, 2014.
- 15) Usman, M., Cresswell, D., Garforth, A., *Petrol. Sci. Tech.*, **29**, 2247 (2011).

要 旨

水素キャリアとしてのメチルシクロヘキサンの繰り返し使用による触媒活性ならびに副生成物への影響

崔 協力^{†1)}, 石井 美香^{†1)}, 辻村 拓^{†1)}, 谷口 貴章^{†2)}, 橋本 康嗣^{†2)}, 難波 哲哉^{†1)}

^{†1)} (国研)産業技術総合研究所 再生可能エネルギー研究センター, 963-0298 福島県郡山市待池台2-2-9

^{†2)} JXTGエネルギー(株)中央技術研究所, 231-0815 横浜市中区千鳥町8番地

再生可能エネルギーの有効活用を目指して、長期貯蔵ならびに大量運搬のため、液体有機ハイドライドは水素キャリアとして注目されている。本稿では、メチルシクロヘキサン (MCH) による水素の貯蔵・放出システムに着目し、MCH 脱水素反応／トルエン (TOL) 水素化反応を繰り返し行った際の触媒活性ならびに副生成物蓄積への影響を検討した。MCH 脱水素反応／TOL 水素化反応は Pt 脱水素触媒と Ni 水素化触媒を用いて、10 回繰り返された。どの工程においても TOL 転化率は 97 % を超

えたが、MCH 転化率は繰り返し使用に伴い 90 % から 84 % ま

で減少した。副生成物の濃度が繰り返し中に 0.7 ~ 0.9 % の範

囲で推移した。副生成物として 70 種類以上の生成物が同定さ

れ、副反応の種類によって脱メチル化物、開環物、5 員環また

は 6 員環化合物を形成する異性化物、二量化物、および多環式

化合物など 6 種類に分類した。10 回繰り返し試験後、脱メチル

化物が最も多いことが分かった。

.....