

By-products accumulation in toluene as a hydrogen carrier during toluene hydrogenation and methylcyclohexane dehydrogenation

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Abstract: Behavior of by-products accumulation in toluene feed by repeated use of it under its hydrogenation and methylcyclohexane dehydrogenation over commercial Pt catalysts was investigated. Almost 70 kinds of by-products were possibility identified from detailed by-products analysis, and categorized them in six kinds of side reaction groups. The products of ring-opening reaction are remarkably increased, and become almost plateau after 7th dehydrogenation process.

Keywords: Toluene hydrogenation, Methylcyclohexane dehydrogenation, By-products.

1. Introduction

Liquid Organic Hydrogen Carriers (LOHC) is attractive materials for the storage and distribution of hydrogen produced from renewable energy. In particular, methylcyclohexane (MCH) as one of LOHC compound is of interest¹⁾, so that we aimed to develop the technology of catalytic reaction process that can respond to the repeated use toluene (TOL) under successive reactions, TOL hydrogenation and MCH dehydrogenation (HD cycle)²⁾. In this study, the behavior of by-products accumulation by the repeated use of TOL over commercial Pt catalyst was investigated.

2. Experimental

10 times HD cycle were carried out by fixed-bed flow reactor. Detailed experimental conditions are shown in Table 1. Over 70 kinds of by-products of each process and their concentration have been analyzed by GC-FID.

Table 1. Reaction conditions of HD cycle

Reaction	Reactor size (mm)	Thermostat of reactor*	Catalyst	H ₂ /TOL ratio	Pressure (MPaG)	LHSV (h ⁻¹)
TOL hydrogenation	Φ17×500 ×2	1) 80 ~ 95°C, 2) 90 ~ 105°C	Pt (0.5)/Al ₂ O ₃	5	0.19	1.9
MCH dehydrogenation	Φ22×570	340°C	Pt (0.5)/Al ₂ O ₃	0.5	0.15	1.9

* 1) and 2) indicate reactor 1 and reactor 2, respectively. These reactors were placed in series.

3. Results and discussion

Original TOL contained 0.13 mol% impurities. The change of by-products concentration in liquid product groups categorized by different side reactions and molecular structures is shown in Figure 1. The 6-membered ring by-products exhibited the largest amount after 1st hydrogenation. these products were slowly increased when HD cycle (1st H ~ 10th D) proceeded. The amount of 6-membered ring by-products increased at dehydrogenation and decreased at hydrogenation. Conversely, the amount of 5-membered ring by-products decreased at dehydrogenation and increased at hydrogenation, though the amounts for 1st D and 10th D were almost same. The products of demethylation and ring-opening reaction were increased almost similarly till 6th dehydrogenation when HD cycle was repeated, however in the 7th hydrogenation, the ring-opening by-products increased remarkably. Compared to demethylation and ring-opening production, small amounts of dimerization by-products were observed, and the by-products group exhibited slight increase.

The polycyclic by-products, such as fluorenes, was formed as a sequential reaction from the dimerization by-products.

The change of reaction conversion, methane emission and increase amounts of by-products from toluene feed is shown in Figure 2. In the HD cycle, while conversions of TOL hydrogenation were maintained at 95%. Conversions of MCH dehydrogenation was fluctuated in the range of 82~90%, and noticeably lower than equilibrium conversion of 96% especially. The methane concentration for all steps of hydrogenation and dehydrogenation was maintained below 100 ppm.

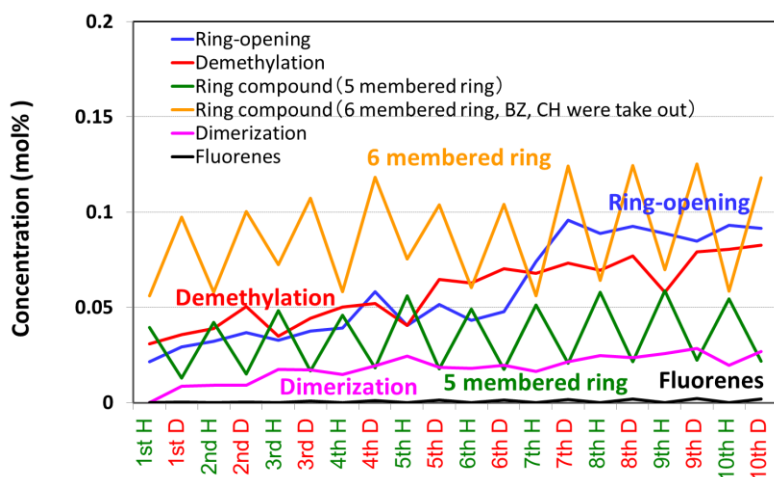


Figure 1. Changes of the amount of by-product groups categorized by different molecular structures in HD cycle

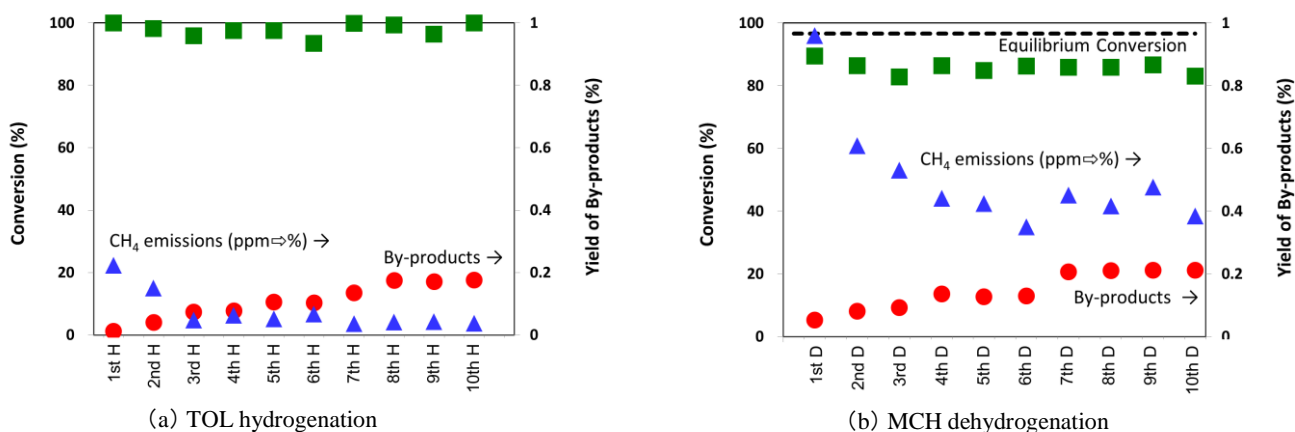


Figure 2. Changes of reaction conversion, CH₄ emission and increase amounts of by-products in HD cycle

4. Conclusions

By-products showed an excellent behavior, increase amounts of concentration for all steps of hydrogenation and dehydrogenation were maintained below 0.2mol%. The products of ring-opening reaction were most remarkable increased compared to other kinds of side reaction groups, and become almost plateau after 7th dehydrogenation process. Conversions of MCH dehydrogenation were fluctuated in the range of 82 ~90%.

References

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