Selective conversion of 2,5-hexanedione to 3-methyl-2-cyclopentenone over solid acid catalyst

Shun Nishimura,[a,*] **Shintaro Ohmatsu,**[a] **Kohki Ebitani**[a]
[a]*Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan*
**Shun Nishimura: +81-(0)-761-51-1149, s_nishim@jaist.ac.jp*

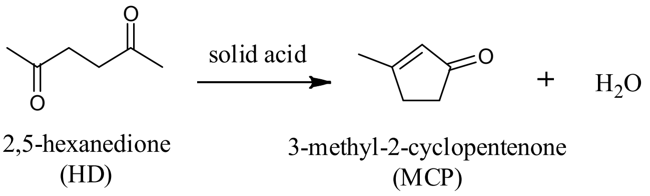
Abstract: 2,5-Hexanedione (HD) is a biomass-based material produced through the 5-hydrxymethyl-2-furaldehyde (HMF) transformation: *i.e.* hydrogenolysis of HMF to 2,5-dimetylfuran (DMF) and successive hydrolysis provides HD. In this study, we have focused on selective intramolecular aldol condensation of HD towards 3-methyl-2-cyclopentenone (MCP) with solid acid catalyst. The produced MCP is one of useful intermediates to serve a variety of natural products and gasoline additives, however, few solid catalytic systems have been investigated in previous reports. We have found out that simple aluminum oxides such as γ-Al_2O_3 and AlOOH gave a significant performance for MCP generation from HD.

Keywords: 2,5-hexanedione, 3-methylcyclopent-2-enone, aluminum oxides.

1. Introduction

Generation of high impacted compounds from biomass resources has been investigated in these decades following to the demand of sustainable development and low carbon society[1-3]. The HMF-based transformations have constructed one of major biomass conversion systems including such as HMF hydrolysis, oxidation, reduction, oxidative/reductive ring-opening, hydrogenolysis and so on.

In this study, we focused on selective conversion of 2,5-hexanedione (HD) to 3-methyl-2-cyclopentenone (MCP) with various solid acid catalysts (**Scheme 1**). The HD is producible through hydrogenolysis of HMF and successive hydrolysis. Although the target material of MCP has been considered as important intermediates for a variety of natural products and gasoline additives, few catalytic systems except for homogeneous NaOH and KOH were reported as conventional way for this transformation[4-5]. Notably, Bell *et al.* recently announced that Mg-Al-O_x catalyst generated from calcination of Mg-Al hydrotalcite at 700 °C afforded 98% yield and selectivity for MCP production from HD[6].



Scheme 1. Selective conversion of 2,5-hexanedione to 3-methyl-2-cyclopentenone.

2. Experimental

Selective conversion of HD to MCP was performed in an ACE pressure tube (18 mL vol.). The mixture of substrate (1.0 mmol), catalyst (100 mg) and solvent (3 mL) was put into the reactor, and stirred at 140 °C for 4 h. The reactant was analyzed by a GC-FID (Shimadzu GC-2014) equipped with a capillary column (Agilent DB-1). Dodecane (0.5 mmol) was used as an internal standard.

In order to identify the type of acid sites on solid catalysts; *i.e.* Brønsted and/or Lewis acid sites, pyridine adsorbed FT-IR was investigated. All samples were pretreated at 150 °C for 1 h under vacuum, and then pyridine introduction was carried out at 100 °C for 30 min. After additional 30 min evacuation for cleaning, FT-IR spectra were collected with a JASCO FT/IR-4700 spectrometer at 100 °C.

Presence of Lewis acid site was also discussed by the reactivity on MPV reduction according to previous report[7]. The reaction was tested with the following conditions: furfural (1.3 mmol), 2-propanol (83 mmol), catalyst (100 mg), temp. (82 °C), and time (24 h).

3. Results and discussion

Table 1. Selective conversion of HD to MCP with solid catalyst.

Catalyst	Conversion of HD (%)	Yield of MCP (%)	Selectivity of MCP (%)
γ-Al_2O_3[a]	91	64	71
AlOOH	56	44	80
$Al(OH)_3$	0	0	0
SiO_2-Al_2O_3[a]	40	4	9
ZSM-5[a]	88	0	0
β-zeolite[a]	84	4	5
Amberlyst-35[b]	92	0	0
Mg-Al hydrotalcite	42	30	70
H_2SO_4[c]	30	0	0

Reaction conditions: HD (1 mmol), catalyst (100 mg, 30 mg[c]), dehydrated 1,4-dioxane (3 mL), temp. (140 °C), time (4 h, 10 min[c]). (a) pretreated at 500 °C for 5 h. (b) Dried at 110 °C.

A variety of solid acid and base catalysts were surveyed for the target reaction (**Table 1**). γ-Al_2O_3 (JRC-ALO-8) and AlOOH (Wako) gave 64% and 44% yield with 71% and 80% selectivity for HD conversion to MCP, respectively. While, on the other hand, $Al(OH)_3$ (KANTO) was completely inactive (0%). The highly-active γ-Al_2O_3 possessed Lewis acidic sites determined by both pyridine-adsorbed IR spectroscopy and MPV reduction. To investigate the side reaction in the case of aluminum oxides, possibility of successive transformation of MCP was examined under same reaction condition. 37% and 10% consumptions of MCP were respectively detected over γ-Al_2O_3 and AlOOH, however, side-reactions were hardly identified by ICP-TOFMS analysis.

SiO_2-Al_2O_3 (JRC-SAH-1) gave only 4% MCP yield with moderate conversion (40%) whereas ZSM-5 zeolite (JRC-Z5-90H(1)) and β-zeolite (JRC-Z-HB150) served 0% yield with high conversion (>84%). Presences of Brønsted acidic sites were detected by pyridine-adsorbed IR spectroscopy in these cases. In addition, commercial protonic resin catalyst of Amberlyst-35 and homogeneous H_2SO_4 catalyst also afforded similar tendency: high conversion (92% or 30%) with no MCP yield. According to these results, Brønsted acidic catalysts seemed to be contributed to high consumption of HD with scarcely few or no yield for MCP production process. The control experiments suggested that these would ascribe to rehydration of HD to DMF proceeded over Brønsted acidic catalyst.

Conventional Brønsted base Mg-Al hydrotalcite (non-calcined, Tomita, Mg/Al = 3)[8] showed 30% yield with 70% selectivity. Other oxides such as MgO, CaO, ZrO_2, WO_3, La_2O_3 and TiO_2 showed no yields with few conversion (< 4%) (these are not shown in **Table 1**). Accordingly, these base and/or oxides were non-effective group for MCP production in compare with aluminum oxides.

4. Conclusions

Lewis acidic γ-Al_2O_3 was found to be the specific solid catalyst to proceed selective transformation of HD toward MCP, and it afforded 64% yield with 71% selectivity.[9] While, presence of Brønsted acidic sites prohibited the target reaction owing to promoting the side reaction of rehydration of HD to DMF.

References

1. R. Putten, J. C. Waal, E. Jong, C. B. Rasrendra, H. J. Heeres, J. G. Vries, Chem. Rev. 113 (2013) 1499.
2. M. Besson, P. Gallezot, C. Pinel, Chem. Rev. 114 (2014) 1827.
3. H. Kobayashi, A. Fukuoka, Green. Chem. 15 (2013) 1740.
4. M. L. Karpinski, D. Nicholas, J. C. Gilbert, Org. Prep. Proced. Int. 27 (1995) 569.
5. L. Bagnell, M. Bliese, T. Cablewski, C. R. Strauss, J. Tsanaktsidis, Aust. J. Chem. 50 (1997) 921.
6. E. R. Sacia, M. H. Deaner, Y. L. Louie, A. T. Bell, Green. Chem. 17 (2015) 2393.
7. M. Shitrotori, S. Nishimura, K. Ebitani, Catal. Sci. Technol. 6 (2016) 8200.
8. S. Nishimura, A. Takagaki, K. Ebitani, Green. Chem. 15 (2013) 2026.
9. S. Nishimura, S. Omatsu, K. Ebitani, *in preparation*.

Acknowledgement

This study was supported by Grant-in-Aid for Young Scientists (A) (Grant No. 17H04966).