High performance of catalytic transfer hydrogenation of biomass-derived unsaturated carbonyl using La_2O_3

Taufik Abdillah Natsir,[a,b,*] **Takayoshi Hara,**[a] **Nobuyuki Ichikuni,**[a] **Shogo Shimazu.**[a]
[a]*Depatment of Applied Chemistry and Biotechnology, Chiba University, Chiba 263-8522, Japan*
[b]*Department of Chemistry, Universitas Gadjah Mada, Sekip Utara Bulaksumur, Yogyakarta 55281, Indonesia.*
**Corresponding author: taufik.abdillah@ugm.ac.id or tanatsir@chiba-u.jp*

Abstract: Single rare earth oxide (La_2O_3) prepared by a simple hydrothermal method and subsequent various heat treatment showed high catalytic activity in the catalytic transfer hydrogenation of furfural. Gas pressure and reaction temperatures influenced the catalytic performance of pretreated La_2O_3. La_2O_3 showed high catalytic performance, producing an unsaturated alcohol (furfuryl alcohol) with high selectivity (98% conversion and 96% selectivity) using 2-propanol as the hydrogen donor at 453 K under N_2 atmosphere (0.8 MPa). The reusability experiment revealed that reactivation of the used catalyst recovered the catalytic performance of La_2O_3.
Keywords: La_2O_3, transfer hydrogenation, furfural.

1. Introduction

The catalytic conversion of biomass and biomass derivative to added value has attracted researchers due to the shortcoming of fossil resources. One of the promising compounds derived from biomass is furfuryl alcohol (FFA), which is essential for producing high-strength fibers, polyurethane foam and elastomers, and conjugated polymers.[1] Furfuryl alcohol is mainly produced industrially from hydrogenation of furfural using Cu-based catalyst, and the most widely used are Cu-Cr catalyst.[2] However, the existence of chromium in this catalyst causes toxicity issues that threaten the environment. Therefore, developing a non-chromium catalyst for selective hydrogenation of furfural to FFA is an interesting pursuit for chemists.[3]

Recently, we reported that treatment of La_2O_3 in various heat, and under various atmosphere affected its catalytic performance in the hydrogenation of furfural to FFA.[3] We also found that the basic sites of the catalyst influenced the catalytic activity. Meanwhile, the acidic sites influenced the selectivity of FFA.

In the present report, we extended our study to optimize the reaction conditions and to study the stability of the catalyst. Results showed that the increase in N_2 pressure and reaction temperature gave comparable results to the catalytic activity. While the presence of $La(OH)_3$ that appeared after the reaction decreased the catalytic activity of the used catalyst. Furthermore, the used La_2O_3 regained its catalytic activity after the heat treatment using the same conditions as the preparation of fresh catalyst.

2. Experimental

To synthesize the catalyst, $La(NO_3)_3$ solution was precipitated at pH 12. The as-precipitated was transferred into an autoclave, which was kept at 423 K for 24 h. After filtered and dried, the as-synthesized was calcined at 923 K and was followed by hydrogen treatment at 673 K (denoted as La_2O_3_ C923_HT673).

3. Results and discussion

The effect of N_2 gas pressure to the catalytic performance of La_2O_3_ C923_HT673 was studied in the range between 0.2 – 1.0 MPa (Table 1, entries 1-5). The increase of N_2 gas pressure promoted furfural conversion and reached an optimum at 0.8 MPa (98% conversion and 96% selectivity, entry 4). The influence of gas pressure was also investigated by using H_2 gas. The catalytic performance of La_2O_3_ C923_HT673 under H_2 (Entry 6) had a similar result with N_2 (99% conversion and 94% selectivity). These results indicated that the catalytic performance of La_2O_3_ C923_HT673 was influenced only by the gas pressure but not by the type of gas being used. The influence of reaction temperature was investigated in the range between 403 K – 453 K as shown in Table 1 (entries 4, 7, and 8). The conversion of furfural increased with increasing the reaction temperatures (403 K ~ 453 K). The transfer of hydrogen from 2-propanol to furfural was accelerated at high reaction temperature.

$La(OH)_3$ phase appeared after the reaction. This indicated that La_2O_3 had been converted to $La(OH)_3$. Phase quantification of the used catalyst was determined from the calibration curve, and showed percentage of La_2O_3 to be 26.3 % while $La(OH)_3$ was 73.7%. The presence of $La(OH)_3$ phase caused the decline in the catalytic activity of the catalyst (68% conversion). Reactivation of the used catalyst using the same condition with fresh catalyst (heat treatment at 923 K, and H_2 treatment at 673 K) recovered the catalytic activity of La_2O_3

4. Conclusions

In conclusion, we have demonstrated the high catalytic performance of La_2O_3 for catalytic transfer hydrogenation of furfural to FFA (98% conversion and 96% selectivity). Gas pressure and reaction temperature influenced the catalytic transfer hydrogenation of this reaction. The decline in catalytic activity of the spent catalyst was caused by the formation of $La(OH)_3$ phase. The catalytic performance of spent catalyst was regained after it was reactivated under the same condition with fresh catalyst.

Table 1. Catalytic transfer hydrogenation of FFR to FFA by La_2O_3 at different initial gas pressures and reaction temperatures

Entry	Reaction temp. (K)	Reaction pressure (MPa)	Conv. (%)	Sel[b] (%)
1	453	0.2	79	94
2	453	0.4	84	91
3	453	0.6	93	80
4	453	0.8	98	96
5	453	1.0	98	80
6	453	0.8[a]	99	94
7	423	0.8	61	96
8	403	0.8	24	98

Reaction conditions: furfural =1.1 mmol, catalyst = 0.15 mmol, 2-propanol = 3 mL, reaction time = 17 h. [a]under H_2 gas. [b]Selectivity of FFA.

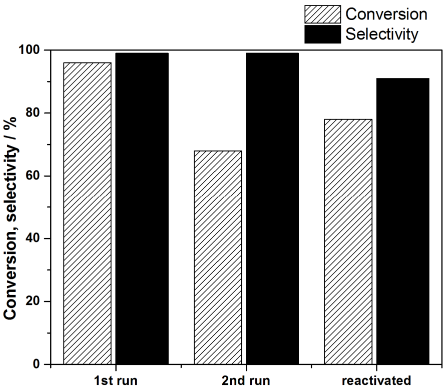

Figure 1. Reusability test of La_2O_3. Reaction conditions: FFR =1.1 mmol, catalyst = 0.15 mmol, N_2 pressure = 0.8 MPa, reaction temperature = 453 K, reaction time = 14 h for La_2O_3.

Acknowledgement

This study was financially supported in part by JSPS KAKENHI Grant Number 15K06565 and JSPS Bilateral Joint Research Project (2014-2017).

References

1 M. Choura, N. M. Belgacem, A. Gandini, *Macromolecules* **1996**, *29*, 3839.
2 X. Li, P. Jia, T. Wang, *ACS Catal.* **2016**, *6*, 7621.
3 T. A. Natsir, T. Hara, N. Ichikuni, S. Shimazu, *Chem. Lett.* **2017**, *46*, 1580.