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One-pot synthesis of 1,3-butanediol by 1,4-anhydroerythritol hydrogenolysis over tungsten-modified platinum on silica catalyst

Received 00th January 20xx, Accepted 00th January 20xx Lujie Liu,^a Takehiro Asano,^a Yoshinao Nakagawa,^{a,b,*} Masazumi Tamura^{a,b} and Keiichi Tomishige^{a,b,*}

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Chemical production of 1,3-butanediol from biomass-derived compounds was first reported by 1,4-anhydroerythritol hydrogenolysis over Pt-WO_x/SiO₂ catalyst. The reaction proceeded by ring opening hydrogenolysis of 1,4-anhydroerythritol followed by selective removal of secondary OH group in 1,2,3-butanetriol, and an overall 1,3-butanediol yield up to 54% was then obtained. The performance of Pt-WO_x/SiO₂ catalyst for 1,4-anhydroerythritol hydrogenolysis was closely correlated with that for glycerol hydrogenolysis to 1,3-propanediol. The optimized Pt-WO_x/SiO₂ (Pt: 4 wt% and W: 0.94 wt%) catalyst showed 57% yield of 1,3-propanediol.

Transformation of biomass derived feedstocks to high valueadded chemicals has been a hot topic over the past few decades since biomass is regarded as a renewable resource for the green chemistry.¹⁻⁶ Diols are widely used as co-monomers in polymers formation, and preparation of ethylene glycol, for example, from cellulose⁷⁻⁹ and propanediols (PrDs) (glycerol selective hydrogenolysis to 1,2-PrD¹⁰ and 1,3-PrD¹¹⁻¹³) via biomass-based hydroconversion is available using heterogeneous metal catalysis. To date, the synthesis of chain butanediols (BuDs) with internal OH group (1,2-, 2,3- and 1,3-BuD) is still of great challenge by catalytic hydrodeoxygenation of biomass-based platform chemicals, and high yield of the aforementioned C4 diols is not reported except cis-didehydroxylation of erythritol to 1,2-BuD.14 1,3-BuD can be used for production of polyurethane and polyester resin as a co-monomer.⁵ At present, acetaldehyde condensation and hydrogenation,¹⁵ and Prins condensation using propylene and formaldehyde followed by hydrolysis¹⁶ are effective systems to obtain 1,3-BuD as well as the biochemical route for preparation of 1,3-BuD.¹⁷ Both our group and other groups have made some attempts in selective conversion of erythritol¹⁸⁻²¹ and 1,4-anhydroerythritol (1,4AHERY)^{14,22-26} as starting substrates since erythritol is easily accessible by fermentation in industrial scale²⁷⁻²⁹ and 1,4-AHERY can be derived from simple dehydration of erythritol.³⁰ 1,4-AHERY is a platform substrate, which can be converted into valuable chemicals by various heterogeneous catalysis systems, as tetrahydrofuran (THF),^{14,31} 1,4-BuD,^{25,26} such 3hydroxytetrahydrofuran (3-HTHF),²² 2-butanol (2-BuOH)²³ and 2,5-dihydrofuran.²⁴ In fact, we have proposed a two-steps route for 1,3-BuD synthesis, including selective hydrodeoxygenation of 1,4-AHERY to 3-HTHF and subsequent hydrogenolysis to 1,3-BuD (Scheme 1, route 1).^{22,32} Combining these two systems to a one-pot process is difficult due to the big difference in reaction conditions such as temperature and solvent. In addition, we have shown that the main product of 1,4-AHERY hydrogenolysis at low conversion is 1,2,3-butanetriol (1,2,3-BuT) over many types of catalysts including Rh/SiO₂, Rh-MO_x/SiO₂ (M = Mo, W, Re), Pt-MoO_x/SiO₂, and Ir-ReO_x/SiO₂.²³ It appears promising to develop a one-pot synthesis of 1,3-BuD by ring opening of 1,4-AHERY to 1,2,3-BuT and selective cleavage of secondary OH group to 1,3-BuD by catalytic regioselective hydrogenolysis (Scheme 1, route 2). To achieve higher yield of 1,3-BuD from 1,4-AHERY, the step of 1,2,3-BuT to 1,3-BuD should proceed over catalyst with high selectivity.



Scheme 1 Proposed reaction pathway of 1,4-AHERY to 1,3-BuD.

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Electronic Supplementary Information (ESI) available: Experimental section, literature survey (Table S1), XRD and XANES spectra (Figs. S1 and S2) and supplementary reaction data (Fig. S3; Tables S2-S7). See DOI: 10.1039/x0xx00000x

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Table 1 Catalytic performance of Pt-WO_x/SiO₂ related catalysts in the 1,4-AHERY hydrogenolysis

| Entry | Catayst | W/Pt | Conv. | Selectivity / % | | | | | | 0.0002112 | |
|-----------------------|--------------------------------------|-------|-------|-----------------|-----------|--------|--------|---------|---------|-----------|--------|
| | | ratio | /% | 1,3-BuD | 1,2,3-BuT | 1-BuOH | 2-BuOH | 1,2-BuD | 2,3-BuD | 3-HTHF | Others |
| 1 | 4 wt% Pt/SiO ₂ | - | <1 | - | - | - | - | - | - | - | - |
| 2 | Pt-WO _x /SiO ₂ | 0.063 | 5 | 22 | 68 | - | 3 | - | <1 | 4 | 2 |
| 3 | | 0.13 | 25 | 24 | 66 | <1 | 4 | 1 | 1 | 3 | 1 |
| 4 | | 0.25 | 60 | 38 | 41 | 2 | 7 | 2 | 5 | 5 | <1 |
| 5 | | 0.5 | 26 | 25 | 60 | 2 | 8 | 2 | 1 | 2 | <1 |
| 6 | | 1 | 5 | 21 | 54 | - | 15 | 1 | 2 | 5 | 2 |
| 7 ^a | WO _x /SiO ₂ | - | <1 | - | - | - | - | - | - | - | - |
| 8 ^b | Physical mixture | - | 33 | 13 | 82 | <1 | 3 | - | 1 | 2 | - |

Reaction conditions: 1,4-AHERY = 0.5 g, $H_2O = 4$ g, $W_{cat} = 0.2$ g, $P(H_2) = 8$ MPa, T = 413 K, t = 24 h.

^a0.94 wt% WO_x/SiO₂. ^bPhysical mixture: 0.2 g of 4 wt% Pt/SiO₂ + 0.2 g of 0.94 wt% WO_x/SiO₂. $t/h = 1 24124481112^{a}1$ 8^b 24^b 4^c 8^c 1 12448148 1 1 24 1 1 1 literature studies were



Fig. 1 Catalytic performance of hydrogenolysis of 1,4-AHERY over the screened catalysts (Noble metal: 4 wt%, M = W, Mo and Re, M/Noble metal = 0.25, molar ratio). Reaction conditions: 1,4-AHERY = 0.5 g, $H_2O = 5$ g, $W_{cat} = 0.1$ g, $P(H_2) = 8$ MPa, T = 413 K, t = 1 h. a: T = 433 K. b: 1,4-AHERY = 1 g, $H_2O = 4$ g, W_{cat} (4 wt% Ir, Re/Ir = 1) = 0.1 g, $P(H_2) = 8$ MPa, T = 393 K.²³ c: Pre-reduction by H_2 flow at 573 K for 1 h.

On the other hand, glycerol hydrogenolysis to 1,3-PrD has been intensively investigated,³³⁻³⁶ which reaction itself is a very important one in biomass refinery and can be a model reaction for 1,2,3-BuT hydrogenolysis to 1,3-BuD. The Pt-based catalysts, especially combined with WOx species (4-38 wt% W in most cases, Table S1), and Ir-based catalysts, particularly promoted by ReO_x species, showed high selectivity to 1,3-PrD (up to ~70%) in glycerol hydrogenolysis.¹¹⁻¹³ There are limited reports for 1,4-AHERY hydrogenolysis over Pt- and Ir-based catalysts. We reported that Ir-ReO_x/SiO₂ catalyst gave 23% selectivity to 1,3-BuD at 63% 1,4-AHERY conversion, while that catalyst showed maximum 38% yield of 1,3-PrD in glycerol hydrogenolysis.23 Yang and Cao et al. recently reported that IrO_x/H-ZSM-5 catalyst converted 1,4-AHERY into THF with 85% selectivity at 64% conversion, while such catalyst selectively converted glycerol to 1,3-PrD at initial stage (75% selectivity) and the maximum 1,3-PrD yield was 28%.³¹ Shishido et al. tested Pt/WO₃/Al₂O₃ catalyst, and the 1,4-AHERY conversion was about 1 order lower than that in glycerol hydrogenolysis with the main product of THF whereas high 1,3-PrD selectivity (~45%) in glycerol conversion was obtained.37,38 The 1,3-BuD yields of these literature studies were quite low, even considering the moderate or high yield of 1,3-PrD from glycerol over the same catalyst. In this work, we developed an effective and reusable heterogeneous Pt-WO_x/SiO₂ catalyst with low W amount (W: 0.94 wt%, Pt/W = 4, molar ratio) for 1,3-BuD production with high yield (54%) by 1,4-AHERY hydrogenolysis route. The catalyst exhibits high 1,3-PrD yield (57%) at relatively low reaction temperature compared to other works for Pt-WO_x catalysts in glycerol hydrogenolysis (Table S1). The performance of 1,4-AHERY hydrogenolysis to 1,3-BuD and that of glycerol to 1,3-PrD over various Pt-WO_x/SiO₂ was closely correlated.

The tungsten modified group 8 noble metals (Pt, Ir, Rh, Ru and Pd) on SiO₂ catalysts were examined with fixed ratio (0.25) of W/noble metal in 1,4-AHERY hydrogenolysis (Fig. 1). Catalysts were prepared by sequential impregnation method and details about reaction procedure are shown in Supporting Information. The 1,3-BuD was only detected over Pt-WO_x/SiO₂ and Ir- WO_x/SiO_2 catalysts whereas other WO_x -modified ones were not effective to obtain the desired 1,3-BuD. The other product over these catalysts was mainly the possible intermediate of 1,2,3-BuT. However, the selectivity to 1,3-BuD was not increased over Ir-WO_x/SiO₂ even at longer reaction time. Next, the Ir-ReO_x/rutile catalyst which is the most active one in glycerol hydrogenolysis to 1,3-PrD¹³ was also tested in 1,4-AHERY hydrogenolysis. The 1,3-BuD yield was less than 20%, and large amount of 2-BuOH was co-produced due to the overhydrogenolysis, which was similar to the case of Ir-ReO-_x/SiO₂ in 1,4-AHERY hydrogenolysis.²³ We further tested catalysts modified with other oxophilic metals (Mo, Re and W) in this reaction. The Pt-MoO_x/SiO₂ showed some activity, but the selectivity was unsatisfactory. In addition, the Rh-WO_x, Pt- ReO_x , Pd-MoO_x and Ir-MoO_x/SiO₂ catalysts gave some activity. About 50% selectivity to 1,2,3-BuT was detected together with certain amount of butanols. However, only trace amount of 1,3-BuD was observed, indicating that the poor regioselectivity over these catalysts and the butanols were produced by hydrogenolysis of 1,2-, 2,3-BuD and/or 3-HTHF. Therefore, the WO_x-modified Pt catalyst was selected for further study. Table 1 lists the effect of W amount at fixed Pt loading amount (4 wt%) on 1,4-AHERY hydrogenolysis over Pt-WO_x/SiO₂. The catalytic performance showed a volcano-type dependence on W amount at the W/Pt ratio from 0.063 to 1 (entries 2-6), and catalyst with

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Fig. 2 Effect of support on the 1,4-AHERY hydrogenolysis over 4 wt% Pt-WO_x based catalysts (W/Pt = 0.25). Reaction conditions: 1,4-AHERY = 0.5 g, H₂O = 4 g, W_{cat} = 0.2 g, $P(H_2)$ = 8 MPa, T = 413 K, t = 24 h.



Fig. 3 Time course of the (A) 1,4-AHERY and (B) glycerol hydrogenolysis over 4 wt% Pt-WO_x/SiO₂ (W/Pt = 0.25). Reaction conditions: 1,4-AHERY = 0.5 g or glycerol = 1 g, H₂O = 4 g, W_{cat} = 0.2 g, $P(H_2)$ = 8 MPa, T = 413 K. The detailed data are provided in Tables S6 and S7.

W/Pt ratio of 0.25 gave the highest activity. The volcano-type dependence on W amount has been also reported for Pt-WO_x based catalysts in cleavage of C-O bond although the activity was generally maximized at relatively high W amount (e.g. 7~8 wt%).37,39 With small amount of W, fewer WO_x clusters are available for 1,4-AHERY to anchor; increasing the W loading amount would lead to higher coverage of WO_x species on Pt metal surface, and thus lower the ability for H₂ activation. In both cases, the activity is decreased. The main products over Pt- WO_x/SiO_2 were 1,3-BuD and 1,2,3-BuT, and the latter is a possible intermediate of 1,3-BuD formation. With higher W/Pt ratio above 0.25, the selectivity to 2-BuOH which is an overhydrogenolysis product, was increased even at decreasing conversion level. The effect of W amount on glycerol hydrogenolysis was also investigated and results are shown in Table S2. The activity trend gave even stronger dependency on W amount in glycerol conversion, and $Pt-WO_x/SiO_2$ (W/Pt = 0.25) was the most active one for both reactants. In the optimization of Ir-ReO_x/SiO₂ catalyst, Mushrif and et al. proposed that the reaction pathway was altered with increasing the Re/Ir ratio.⁴⁰ Higher coverage of ReO_x clusters on Ir particles facilitated thermodynamically preferred product of 1,2-PrD due to the Brønsted acidic ReO_x clusters. However, such phenomena was not observed, and the selectivity to 1,2-PrD + 2-PrOH was even decreased at W/Pt ratio from 0.13 to 0.5 (Table S2). That means that the dominant route was not changed over catalysts modified by different W amount. Then we compared the activity over these catalysts at same conversion level (25%) in

1,4-AHERY hydrogenolysis, the total selectivity to 2_{10} BuO H = 1,2,3-BuT was almost constant (Table SP) The 2-Did was also prone to be produced at higher W amount and the selectivity to 1,3-BuD + 1,2,3-BuT became lower. Considering that 2-BuOH is a by-product in overhydrogenolysis of 1,3-BuD as discussed later, it seems that the catalyst structure tuned by W amount affects each reaction step to a different extent in 1,4-AHERY hydrogenolysis. Both Pt/SiO₂ and WO_x/SiO₂ hardly catalyzed the 1,4-AHERY hydrogenolysis, and the physical

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catalyzed the 1,4-AHERY hydrogenolysis, and the physical mixture one (entry 8) gave much lower 1,3-BuD yield relative to the 4 wt% Pt-WO_x/SiO₂ (W/Pt = 0.25) catalyst. The aforementioned results suggest that the synergistic effect between Pt and WO_x species has profound influence on the catalytic performance, and such synergy is sensitive to W amount.

XRD patterns of related $Pt-WO_x/SiO_2$ catalysts showed that the bulk Pt was in metallic state after calcination or catalytic use. The Pt dispersion was promoted by addition of W, and the WO₃ species was solely observed at W/Pt ratio of 1 over 4 wt% Pt-WO_x/SiO₂ (Fig. S1). However, the change of Pt particle size was small in comparison with the activity difference (Table 1). Therefore the synergy between Pt and WO_x species whose structure was changed with the W amount is responsible for the hydrogenolysis catalysis. The average particle size of Pt of physical mixture sample (Pt/SiO₂ + WO_x/SiO₂) and standard catalyst (Pt-WO_x/SiO₂) after reaction was comparable (~4.4 nm), which was smaller than the Pt/SiO₂ (7.0 nm). Probably, the presence of some leachable WO_x species suppresses the Pt particles aggregation during the reduction and reaction. The XANES spectra were further employed to determine the valence of both Pt and W over $Pt-WO_x/SiO_2$ (4 wt% Pt, W/Pt = 0.25) catalyst (Fig. S2). The Pt species were partially reduced after calcination, and transformed into Pt⁰ after reduction (L, 473). The W L₃-edge XANES spectrum of calcined catalyst was similar to WO₃ and precursor (NH₄)₆H₂W₁₂O₄₀·nH₂O. After reduction, the white line intensity was between WO₂ and WO₃, indicating that a small amount of W was reduced.

The support also has drastic effect on the activity of bimetallic catalysts based on our previous reports.13,14 Therefore the activity of Pt-WO_x (Pt: 4 wt%, W/Pt = 0.25) pairs dispersed on a series of supports was then investigated (Fig. 2). SiO₂ was by far the best support in views of both activity and selectivity. Activated carbon, MgO, H-ZSM-5, CeO₂, ZrO₂ and Al₂O₃ supported Pt-WO_x catalysts gave almost no activity. Probably, the Pt and WO_x species were individually dispersed on these supports since no activity was also observed over Pt/SiO₂ or WO_x/SiO₂ catalyst. The conversion over rutile TiO₂ supported catalyst was higher than that over P25 TiO₂. With respect to the products distribution, the selectivity to 1,3-BuD + 1,2,3-BuT was almost the same over SiO₂ and TiO₂ support. However, 2-BuOH was more favourable to produce over TiO₂ supported catalysts even at lower conversion level. This result implies that the overhydrogenolysis decreases the 1,3-BuD yield. The support effect on glycerol hydrogenolysis was consistent with that on 1,4-AHERY (Fig. S3). The overhydrogenolysis products of 1-PrOH and propane with high proportion were detected over TiO₂ supported catalysts, decreasing the 1,3-PrD selectivity. In some

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cases of Pt-WO_x (W: \geq 8 wt%) supported on ZrO₂ and Al₂O₃ catalysts, they were active in glycerol hydrogenolysis to 1,3-PrD. $^{35,36,41\cdot43}$ The much lower activity in our case may be due to the small W amount on ZrO₂ and Al₂O₃ support.

We compared the hydrogenolysis of 1,4-AHERY and glycerol activities. Fig. 3A presents the time course of 1,4-AHERY hydrogenolysis. At short reaction time, the main product was 1,2,3-BuT, and another C-O hydrogenolysis product 3-HTHF was hardly observed. The selectivity to 1,3-BuD was increased and that to 1,2,3-BuT was decreased with the reaction progress. The maximum 1,3-BuD yield was 54% at 80 h, which was the highest value among one-pot synthesis using biomass-derived chemicals. It is an alternative green route to produce 1,3-BuD since the yield is comparable to the reported tandem reaction route by Prins condensation using propylene and formaldehyde and followed by hydrolysis (1,3-BuD yield: 60%) over CeO2 catalyst.¹⁶ The time course of glycerol hydrogenolysis is also shown in Fig. 3B. The highest 1,3-PrD yield was 57% at 24 h and the maximum 1,3-PrD productivity ($P_{1,3-PrD}$) was 4.8 g g_{Pt}^{-1} h⁻¹ at 82% conversion and 64% selectivity to 1,3-PrD (12 h), which was in top level among all the reported Pt-WO_x based systems (Table S1). Both high 1,3-PrD yield and high productivity can be achieved over Pt-WO_x/SiO₂ even with such low W amount. The overhydrogenolysis of 1,3-PrD to 1-PrOH was suppressed while that of 1,3-BuD to BuOHs gradually proceeded. The tendency of easier overhydrogenolysis in 1,4-AHERY than glycerol might cause the low yield of 1,3-BuD in the previous studies. Moreover, the Pt-WO_x/SiO₂ catalyst can be reused in 1,4-AHERY hydrogenolysis at least three times without decreasing of activity or selectivity (Table S4). The leaching of Pt was negligible (Table S5) in the solution after catalytic usage. Although small amount of leached WO_x species was detected, it became smaller in the repeated uses. Considering the stable activity in reuses, the loss of W has little effect on the active site of Pt-WO_x/SiO₂.

The optimized Pt-WO_x/SiO₂ (4 wt% Pt, W/Pt = 0.25) catalyst was applied to the hydrogenolysis of related alcohols (Table 2). In the case of triols (entries 2 and 3) hydrogenolysis, 1,2,4- has higher activity than that of 1,2,3-BuT. It can be explained by the higher steric hindrance between 1,2,3-BuT and active site over catalyst surface. The neighboring OH group to the primary OH group possesses higher reactivity (entries 4-7 and 12-13), and cleavage of C-O bond is difficult to proceed over mono-alcohols (entries 8-9). Hydrogenolysis of 3-HTHF gave high selectivity to 1,3-BuD (90%, entry 10) at relatively high conversion level (40%). Both 1,3-PrD and 1,3-BuD have lower reactivity, which is consistent with the obtained high yield (entries 5 and 13). The

overhydrogenolysis of 1,3-PrD was slower than that of 1,3-BuD This result agrees with the conversion of the co overhydrogenolysis of 1,3-BuD was more favorable relative to 1,3-PrD (Fig. 3). An interesting point is that the hydrogenolysis of 1,3-BuD gave 2-BuOH as the main product (entry 5, 78% selectivity). This result indicates that the carbenium ion with the assistance of Brønsted acidic sites is not involved in the C-O bond dissociation in 1,3-BuD, and further study is required to elucidate the reaction mechanism. For erythritol hydrogenolysis, 1,4-BuD was the main product. The conversion routes from erythritol using Pt-WOx/SiO2 are summarized in Scheme 2.

Conclusions

In conclusion, the optimized Pt-WOx/SiO2 with low W loading amount was an effective catalyst for 1,4-AHERY hydrogenolysis to 1,3-BuD. Ir-based catalysts such as Ir-ReO_x/SiO₂ and Ir-ReO_x/rutile were difficult to give high yield of 1,3-BuD due to the overhydrogenolysis to butanols. The reaction is composed of 1,4-AHERY to 1,2,3-BuT and successive hydrogenolysis of 1,2,3-BuT to 1,3-BuD. The performance of Pt-WO_x catalysts for 1,4-AHERY hydrogenolysis to 1,3-BuD was significantly related to that for glycerol hydrogenolysis to 1,3-PrD. The Pt-WO_x catalysts with higher activity and selectivity in glycerol hydrogenolysis showed also high performance in 1,4-AHERY hydrogenolysis to 1,3-BuD. The highest yield of 1,3-BuD and 1,3-PrD from 1,4-AHERY and glycerol was 54% and 57%, respectively. The W amount much affected the activity, showing volcano-curve dependence. On the other hand, Pt particle size was not so changed by the W amount. The synergy of Pt particles and WO_x species should be present, and further study is ongoing to clarify the catalyst structure and reaction mechanism.



Scheme 2 Reaction routes of 1,4-AHERY and erythritol over 4 wt% Pt-WO_x/SiO₂ (W/Pt = 0.25) catalyst.

| Table 2 Catalytic performance of 4 wt% Pt-WO | /SiO ₂ (W/Pt= 0.25) catalyst in the h | nydrogenolysis of related alcoho |
|--|--|----------------------------------|
|--|--|----------------------------------|

| Entry | Substrate | Conv. / % | Products (selectivity (%)) |
|-------|-----------|-----------|---|
| 1 | 1,4-AHERY | 60 | 1,2,3-BuT (41), 1,3-BuD (38), 1,2-BuD (2), 2,3-BuD (5), 2-BuOH (7), 1-BuOH (2), 3-HTHF (5), |
| | | | others (<1) |
| 2 | 1,2,3-BuT | 34 | 1,3-BuD (67), 1,2-BuD (<1), 2,3-BuD (10), 2-BuOH (14), 1-BuOH (8), others (2) |
| 3 | 1,2,4-BuT | 99 | 1,4-BuD (71), 1,3-BuD (8), 2-BuOH (1), 1-BuOH (18), others (2) |
| 4 | 1,4-BuD | 14 | 1-BuOH (97), others (3) |
| 5 | 1,3-BuD | 12 | 2-BuOH (78), 1-BuOH (21), others (1) |
| 6 | 1,2-BuD | 97 | 1-BuOH (92), 2-BuOH (7), others (<1) |

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| 7 | 2,3-BuD | 8 | 2-BuOH (93), butanone (6), n-butane (1) View Article Online |
|-----------------------|------------|----|---|
| 8 ^a | 2-BuOH | <1 | Butanone (61), n-butane (39) DOI: 10.1039/D0GC00244E |
| 9 ^a | 1-BuOH | 1 | Butyraldehyde (12), n-butane (88) |
| 10 | 3-HTHF | 40 | 1,3-BuD (90), 2-BuOH (4), 1-BuOH (4), others (2) |
| 11 ^b | Glycerol | 56 | 1,3-PrD (65), 1,2-PrD (4), 1-PrOH (17), 2-PrOH (12), acetone (1), propane (1) |
| 12 ^b | 1,2-PrD | 60 | 1-PrOH (88), 2-PrOH (9), acetone (<1), propane (2) |
| 13 ^b | 1,3-PrD | 8 | 1-PrOH (96), propane (4) |
| 14 | Erythritol | 83 | 1,2,4-BuT (24), 1,2,3-BuT (12), 1,4-BuD (40), 1,3-BuD (13), 1,2-BuD (1), 2,3-BuD (<1), 1-BuOH |
| | | | (6), 2-BuOH (4) |

Reaction conditions: Substrate = 0.5 g, $H_2O = 4$ g, $W_{cat} = 0.2$ g, $P(H_2) = 8$ MPa, T = 413 K, t = 24 h.

a: *t* = 48 h. b: substrate = 1 g, *t* = 8 h.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem. Int. Ed.*, 2007, **46**, 7164-7183.
- 2 A. Corma, S. Iborra and A. Velty, Chem. Rev., 2007, 107, 2411-2502.
- 3 P. Gallezot, Chem. Soc. Rev., 2012, 41, 1538-1558.
- 4 M. Besson, P. Gallezot and C. Pinel, *Chem. Rev.*, 2014, **114**, 1827-1870.
- 5 L. Wu, T. Moteki, Amit A. Gokhale, David W. Flaherty and F. D. Toste, *Chem*, 2016, **1**, 32-58.
- 6 K. Tomishige, Y. Nakagawa and M. Tamura, *Green Chem.*, 2017, **19**, 2876-2924.
- 7 N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang and J. G. Chen, *Angew. Chem. Int. Ed.*, 2008, **47**, 8510-8513.
- 8 Y. Liu, C. Luo and H. Liu, Angew. Chem. Int. Ed., 2012, **51**, 3249-3253.
- 9 A. Wang and T. Zhang, Acc. Chem. Res., 2013, 46, 1377-1386.
- 10 H. Zhao, L. Zheng, X. Li, P. Chen and Z. Hou, *Catal. Today*, 2019, DOI: https://doi.org/10.1016/j.cattod.2019.03.011.
- 11 Y. Nakagawa, Y. Shinmi, S. Koso and K. Tomishige, *J. Catal.*, 2010, **272**, 191-194.
- 12 L. Liu, S. Kawakami, Y. Nakagawa, M. Tamura and K. Tomishige, *Appl. Catal. B*, 2019, 117775.
- 13 L. J. Liu, T. Asano, Y. Nakagawa, M. Tamura, K. Okumura and K. Tomishige, ACS Catal., 2019, **9**, 10913-10930.
- 14 N. Ota, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, Angew. Chem. Int. Ed., 2015, 54, 1897-1900.
- 15 Y. Tsuji and K. Tagawa, US 6376725B1, 2002.
- 16 Y. Wang, F. Wang, Q. Song, Q. Xin, S. Xu and J. Xu, J. Am. Chem. Soc., 2013, 135, 1506-1515.
- 17 A. Matsuyama, H. Yamamoto, N. Kawada and Y. Kobayashi, J. *Mol. Catal. B*, 2001, **11**, 513-521.
- 18 Y. Amada, H. Watanabe, Y. Hirai, Y. Kajikawa, Y. Nakagawa and K. Tomishige, *ChemSusChem*, 2012, **5**, 1991-1999.
- 19 A. Said, D. Da Silva Perez, N. Perret, C. Pinel and M. Besson, *ChemCatChem*, 2017, 9, 2768-2783.

- 20. A. Sadier, N. Perret, D. Da Silva Perez, M. Besson and C. Pinel, *Appl. Catal. A*, 2019, **586**, 117213.
- 21 Y. Nakagawa, S. Tazawa, T. M. Wang, M. Tamura, N. Hiyoshi, K. Okumura and K. Tomishige, ACS Catal., 2018, 8, 584-595.
- 22 Y. Amada, N. Ota, M. Tamura, Y. Nakagawa and K. Tomishige, *ChemSusChem*, 2014, 7, 2185-2192.
- 23 T. Arai, M. Tamura, Y. Nakagawa and K. Tomishige, ChemSusChem, 2016, 9, 1680-1688.
- 24 L. Sandbrink, K. Beckerle, I. Meiners, R. Liffmann, K. Rahimi, J. Okuda and R. Palkovits, *ChemSusChem*, 2017, **10**, 1375-1379.
- 25 T. M. Wang, S. B. Liu, M. Tamura, Y. Nakagawa, N. Hiyoshi and K. Tomishige, *Green Chem.*, 2018, **20**, 2547-2557.
- 26 T. Wang, M. Tamura, Y. Nakagawa and K. Tomishige, ChemSusChem, 2019, 12, 3615-3626.
- 27 M. Jeya, K.-M. Lee, M. K. Tiwari, J.-S. Kim, P. Gunasekaran, S.-Y. Kim, I.-W. Kim and J.-K. Lee, *Appl. Microbiol. Biotechnol.*, 2009, 83, 225-231.
- 28 Y. Kobayashi, H. Iwata, D. Mizushima, J. Ogihara and T. Kasumi, Lett. Appl. Microbiol., 2015, **60**, 475-480.
- 29 Y. Nakagawa, T. Kasumi, J. Ogihara, M. Tamura, T. Arai and K. Tomishige, ACS Omega, 2020, 5, 2520-2530.
- 30 E. Arceo, P. Marsden, R. G. Bergman and J. A. Ellman, *Chem. Commun.*, 2009, DOI: 10.1039/B907746D, 3357-3359.
- 31 X. Wan, Q. Zhang, M. Zhu, Y. Zhao, Y. Liu, C. Zhou, Y. Yang and Y. Cao, J. Catal., 2019, 375, 339-350.
- 32 K. Chen, K. Mori, H. Watanabe, Y. Nakagawa and K. Tomishige, J. *Catal.*, 2012, **294**, 171-183.
- 33 M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. Della Pina, *Angew. Chem. Int. Ed.*, 2007, **46**, 4434-4440.
- 34 J. ten Dam and U. Hanefeld, ChemSusChem, 2011, 4, 1017-1034.
- 35 Y. Nakagawa, M. Tamura and K. Tomishige, J. Mater. Chem. A, 2014, 2, 6688-6702.
- 36 D. Sun, Y. Yamada, S. Sato and W. Ueda, *Appl. Catal. B*, 2016, **193**, 75-92.
- 37 T. Aihara, H. Miura and T. Shishido, *Catal. Today*, 2019, DOI: https://doi.org/10.1016/j.cattod.2019.10.008.
- 38 T. Aihara, H. Kobayashi, S. Feng, H. Miura and T. Shishido, *Chem. Lett.*, 2017, **46**, 1497-1500.
- 39 N. Lei, X. Zhao, B. Hou, M. Yang, M. Zhou, F. Liu, A. Wang and T. Zhang, *ChemCatChem*, 2019, **11**, 3903-3912.
- 40 J. J. Varghese, L. Cao, C. Robertson, Y. Yang, L. F. Gladden, A. A. Lapkin and S. H. Mushrif, *ACS Catal.*, 2019, **9**, 485-503.
- 41 S. García-Fernández, I. Gandarias, J. Requies, F. Soulimani, P. L. Arias and B. M. Weckhuysen, *Appl. Catal. B*, 2017, **204**, 260-272.
- 42 W. Zhou, J. Luo, Y. Wang, J. Liu, Y. Zhao, S. Wang and X. Ma, *Appl. Catal. B*, 2019, **242**, 410-421.
- 43 Y. Fan, S. Cheng, H. Wang, J. Tian, S. Xie, Y. Pei, M. Qiao and B. Zong, *Appl. Catal. B*, 2017, **217**, 331-341.



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