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Catalysis

One-Step Production of 1,3-Butadiene from 2,3-Butanediol Dehydration

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Abstract: We report the direct production of 1,3-butadiene from the dehydration of 2,3-butandiol by using alumina as catalyst. Under optimized kinetic reaction conditions, the production of methyl ethyl ketone and isobutyraldehyde, formed via the pinacol–pinacolone rearrangement, was markedly reduced and almost 80% selectivity to 1,3-butadiene and 1,3-butadiene could be achieved. The presence of water plays a critical role in the inhibition of oligomerization. The amphoteric nature of γ-Al_2O_3 was identified as important and this contributed to the improved catalytic selectivity when compared with other acidic catalysts.

The use of renewable biomass as a resource for chemical and fuel production has been gaining increasing attention during the last two decades. This is in response to the present global challenge related to the use of fossil fuels and the environmental problems to which their use may contribute. However, installed production capacity based on renewable resources has not reached the levels anticipated for economic reasons and it has increased at a slower rate than originally forecast.[1] One of the key problems is the production of vast amounts of lower value by-products which have limited applications, for instance, glycerol generated from biodiesel production and butanediols generated from biomass fermentation or wood hydrolysis. These by-products potentially make the overall process less efficient and non-profitable.[2] Therefore, the development of value-added uses for the crude biomass-derived by-products or the so-called ‘biomass waste’ will contribute to the viability of the nascent biomass industry.[3] Besides the reduction of waste with a reduced impact on the environment, the recovery of energy and useful feedstocks could make these processes economically practical and competitive against present industrial processes based on readily available fossil fuels.

Recent work has revealed the potential of 2,3-butandiol (BDO) as a promising C_4 platform chemical for use in a variety of industrial applications.[4,5] BDO had been used as the precursor to produce deacetyl, butenes, or 1,3 butadiene before the availability of processes based on the ready availability of inexpensive fossil hydrocarbons were introduced in the 1950s. At present, BDO has only limited industrial applications as a food flavor additive.[6] However, the development of the biomass industry and the abundance of BDO as a by-product have reignited interest in the catalytic conversion of BDO, in particular its dehydration to 1,3-butadiene (BDE). At present, attempts to directly produce BDE with a high yield have failed and the reaction to methyl ethyl ketone, the thermodynamically preferred product, always predominates.[7–9] The mechanism is well understood since the consecutive dehydration of the adjacent two hydroxyl groups leads to an enol which readily forms methyl ethyl ketone (MEK). To achieve high yields of the required product, a two-step process has been designed to convert the diol into the diene by using an acid as an esterifying agent, or catalytic reductive deoxygenation in the presence of H_2 has been used.[10–12] Both processes are not environmentally benign and make industrial production less attractive due to usage of either a stoichiometric acid or a reductant. In addition, biomass-derived polyols are formed at low concentrations in aqueous solution. Refining these crude aqueous solutions, using distillation or membrane separation, is an endothermic reaction requiring a high-energy input, which also hinders the overall potential catalytic conversion process.[13,14]

Here we report a facile method to produce BDE with almost 100% selectivity via the direct dehydration of aqueous BDO using a commercial alumina catalyst. High selectivity to butadiene is achieved by using high flow rates and a smaller amount of catalysts. Our work suggests that under these optimized kinetic reaction conditions the consecutive dehydroxylation via 1,2-elimination to BDE by an E2 mechanism is favored.

The activities for the dehydration of BDO (10 wt%) using a range of catalysts were investigated (Table 1). In most cases, by using a relatively large amount of catalyst (0.5 g), the major product was always MEK, which was produced via partial dehydration followed by the pinacol–pinacolone rearrangement (Equations 1–5).[15] The major by-product was isobutyraldehyde (IBA), which also generated via the pinacol–pinacolone rearrangement (Equations 1, 2, 6–8). BDE was only observed as a minor product for almost all catalysts, except γ-Al_2O_3, where BDE selectivity was 21% at 350 °C (Table 1, entry 13). This was almost double the selectivity observed using bentonite and

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Table 1. Catalytic performance of various oxides catalysts.[a]

	Catalyst	Temp. [°C]	Conv. [%]	Selec. [%] BDE	IBA	MEK	BTO	Enenol	Carbon balance [%]
1	SiWO/SiO_2	350	100	3.7	5.1	91.1	–	–	98
2	SiWO/SiO_2	260	95	0.5	10	89	–	–	80
3	SiO_2	350	95	13	17	70	–	–	100
4	SiO_2	260	94	6.4	12	81	–	–	95
5	bentonite	350	95	13	17	70	–	–	99
6	bentonite	260	60	2.5	14	77	7.5	–	102
7	CeO_2	350	94	1.1	15	84	–	–	100
8	SAB-6	350	98	7	9	84	–	–	75
9	MoO_3	350	98	3.8	8	74	6	7	75
10	WO_3	350	86	2	12	80	3	2	80
11	α-Al_2O_3	350	97	18	12	70	–	–	100
12	α-Al_2O_3	260	34	7.9		83	–	–	100
13	γ-Al_2O_3	350	99	21	3	73	–	–	97
14	γ-Al_2O_3	260	99	7	5	80	4	4	96
15	quatz wool	350	0.1		45	55	–	–	100
16	SiC	350	0						
17	graphite	350	0						

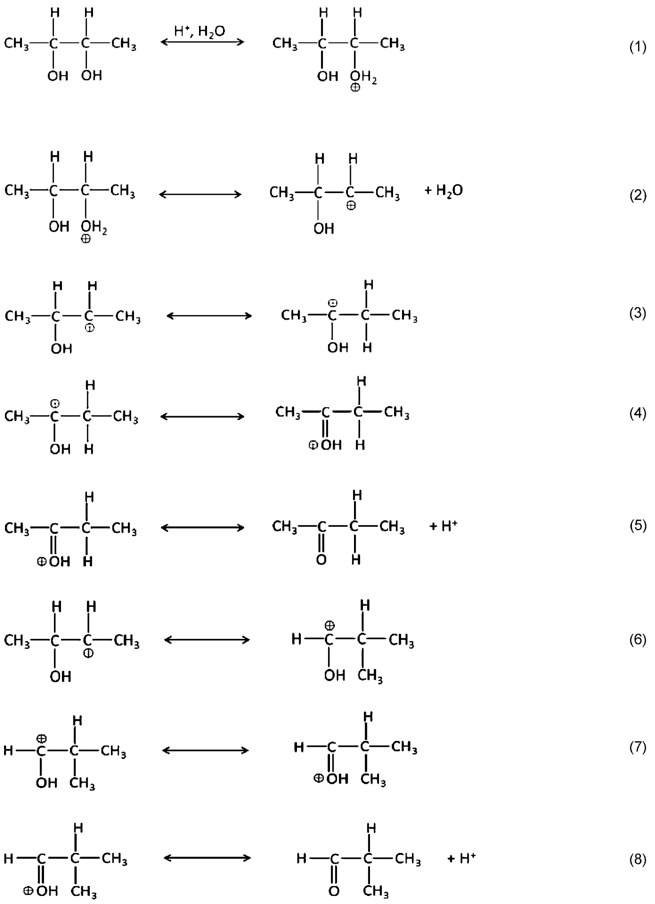
[a] Reaction conditions: 10 wt% BDO, 0.02 mL min^{-1}; 75 mL min^{-1} Ar, 500 mg catalysts, BDE, IBA, MEK, BTO, and enenol represent 1,3-butadiene, isobutyraldehyde, methyl ethyl ketone, 3-buten-2-ol and other butenols (2-buten-1-ol and 3-buten-1-ol), respectively.

SiO_2 under the identical conditions (Table 1, entries 3 and 5). Compared to γ-Al_2O_3, α-Al_2O_3 showed lower productivity of BDE and much higher productivity of IBA at 350 °C (Table 1, entry 11). At a lower temperature (260 °C), the selectivity to BDE when using γ-Al_2O_3 decreased markedly to 7% at almost complete conversion. At 260 °C, we investigated the influence of the BDO concentration on the catalytic performance of γ-Al_2O_3 and complete conversion of BDO was always observed (Table 2). However, the use of 100% BDO does not favor the overall catalytic performance as a low carbon balance was observed (Table 2, entry 1), which could be attributed to the production of di- and tri-oligomers which remained on the catalyst. Addition of a small amount of water (5 wt%) significantly improved the carbon balance from 86% to 96% (Table 2, entry 2). No loss in carbon balance was observed upon further dilution even with high levels of water (i.e. 10 wt% BDO). This confirmed that the presence of water was key for the inhibition of oligomerization.[16]

Table 2. Catalytic performance of Υ-Al_2O_3 at different BDO concentrations.[a]

Catalyst	Conc. [%]	Conv [%]	BDE	IBA	Selec.% MEK	BTO	Enenol	Carbon balance [%]
γ-Al_2O_3	100	96	4	4	90	2	–	87
	95	99	5	4	89	2	–	96
	50	100	7	3	89	0	0	100
	10	99	7	5	80	4	4	96

[a] Reaction conditions: 10 wt% BDO, 0.02 mL min^{-1}; 75 mL min^{-1} Ar, 500 mg catalysts.



The use of alumina as a catalyst for the dehydration of BDO has been reported previously,[16] when 42% selectivity to BDE with 100% BDO conversion was obtained in the presence of H_2. In our case we do not require the presence of H_2 to achieve higher selectivities. Generally, only very limited work can be found over the past 80 years concerning the selective production of BDE from BDO dehydration, apart from the use of thoria in 1945, which has never been used commercially due to the radioactive nature of the catalyst.[7] Therefore, there is no previous mechanistic work on the production of BDE via stepwise dehydration of BDO. With other oxides such as MoO_3 and WO_3, low carbon balances were observed due to the production of cracking products, for example, propene and propane. This suggests a negative role of redox-active catalysts in the dehydration reaction, which could lead to C–C bond fission.

We noted that, even at lower temperature (260 °C), almost 100% conversion could be obtained with γ-Al_2O_3 (Table 1, entry 14). Clearly this indicated that we were using too much catalyst and the reaction was not being operated under kinetic reaction conditions. Hence, we decreased the amount of the catalyst from 500 mg to 3 mg (Table 3, entry 1 to 4). For comparison, we also tested other oxides and acid catalysts under the identical conditions. Obviously, employment of lower amounts of the catalysts led to lower conversions of BDO. Simultaneously, selectivity to butadiene increased markedly. This suggested that the presence of diffusion control or strong

Table 3. Catalytic activities of oxides and acid catalyst with different catalyst amount.[a]

	Catalyst	Mass [mg]	Conv [%]	Selec. % BDE	IBA	MEK	BTO	Enenol	Carbon balance [%]
1	γ-Al_2O_3	500	99	21	3	73	–	–	97
2		40	100	22	13	65	–	–	100
3		6	35	36	23	46	–	–	100
4		3	20	50		47	–	–	98
5	SiO_2	500	100	3.7	5.1	91.1	–	–	98
6		40	100	16.7	14	69	–	–	100
7		10	23	17		82	–	–	98
8		3	6	21	30	49	–	–	99
9	SiWO	500	100	3	6	89	–	–	97
10		40	90	6	36	55	–	–	97
11		3	14	10	30	60	–	–	98
12	α-Al_2O_3	500	97	17	12	69	–	–	100
13		5	67	23	9	67	–	–	95
14		3	25	26	24	50	–	–	99

[a] Reaction conditions: 10 wt% BDO, 0.02 mL min^{-1}; 75 mL min^{-1} Ar, catalysts, 350 °C.

adsorption/re-adsorption, which could reduce the production of butadiene was present when using large amounts of the catalyst. The best selectivity of 50% to BDE was still obtained by using γ-Al_2O_3. The difference in catalytic performance between γ-Al_2O_3 and α-Al_2O_3 was also observed; while the former favored production of BDE and MEK, the latter produced MEK, BDE, as well as IBA. This suggests that moderate acidity is the key factor for the selective dehydration of BDO. Reproducibility of the catalytic performance of γ-Al_2O_3 was also investigated which confirms the low variability in the results using three independent tests (Table 4).

Table 4. Catalytic performance of Υ-Al_2O_3 at different batch.[a]

Catalyst	Batch	Conv. [%]	Selec. [%] BDE	IBA	MEK	BTO	Enenol	Mass balance [%]
γ-Al_2O_3	1	20	50		47		–	98
	2	19	53		47		–	96
	3	21	52		48		–	100
blank	1	0	0		–		–	101
	2	0	0		–		–	100
	3	0	0		–		–	100
SiC[b]	1	1	1		–		–	99
	2	2	2		–		–	98
	3	1.5	–		–		–	98.5[c]

[a] Reaction conditions: 10 wt% BDO, 0.02 mL min^{-1}, 3 mg γ-Al_2O_3, 350 °C. [b] The whole reactor was filled with SiC. [b] No production of BDE, IBA or other products was identified.

To reduce the re-adsorption and diffusion-control, we adjusted the contact times by changing the carrier gas flow rate from 15 mL min^{-1} to 300 mL min^{-1} under the same reaction conditions using 3 mg γ-Al_2O_3 (Table 5 entry 1 to 9, and Figure 1). At the lowest flow rate, about 50% conversion of BDO was observed but with only 10% selectivity to BDE. As the flow rate was increased to 150 mL min^{-1}, the selectivity to BDE increased to 60% and the conversion decreased to 18%. However, with the highest flow rate, the selectivity to BDE did not increase, but decreased to 40% with the production of 3-buten-2-ol (BTO). No production of MEK was observed with the highest flow rate of 300 mL min^{-1}. This suggested that the production of BDE came from further dehydration of BTO, generated via a β-hydride elimination from the terminal methyl group. In this case, production of MEK via the pinacol–pinacolone rearrangement decreased with higher flow rate. This suggests strong dependence of BDE and MEK on the flow rate should be associated with different reaction pathways. Moreover, we found that the higher flow rates also favored the production of BDE by using other catalysts, such as α-Al_2O_3 and silica tungstic acid. This suggests that this is a general trend, correlated with the production of BDE via a consecutive two-step dihydroxylation process (Scheme 1), which can be catalyzed by the acidic active sites in these catalysts. However, the stronger acidity of silicotungstic acid does not favor the production of BDE,[17] which suggests moderate acidity is the key requirement for BDE formation. It is possible that stronger acidity leads to the isomerization reactions and the production of MEK and IBA.

Table 5. Catalytic performance of various oxides catalysts as function of flow rate.[a]

	Catalyst	Flow rate [mL min^{-1}]	Conv. [%]	Selec. [%] BDE	IBA	MEK	BTO	Enenol	Carbon Balance [%]
1	γ-Al_2O_3	15	54	10	8	81			98
2		30	45	18		81			99
3		45	43	20	20	61			97
4		60	30	35	20	45			97
5		75	20	50		47			98
6		100	18	55	12	32			97
7		150	16	60	11	29			95
8		200	13	60	13	11	15		97
9		300	11	41	19	0	40		96
10	SiWO	75	14	10	30	60			101
11		300	2.2	29	31	36	5		99
12	α-Al_2O_3	75	25	26	24	50			99
13		300	6	32	34	30	4		98

[a] Reaction conditions: 10 wt% BDO, 0.02 mL min^{-1}, 3 mg catalysts, 350 °C

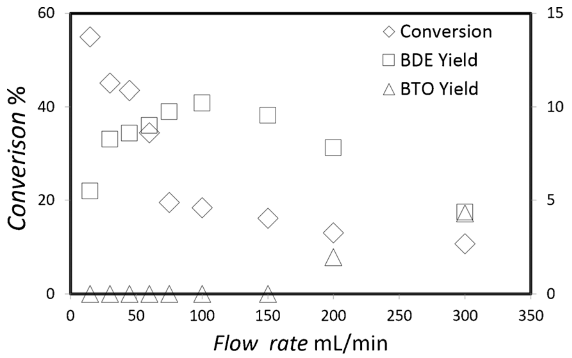
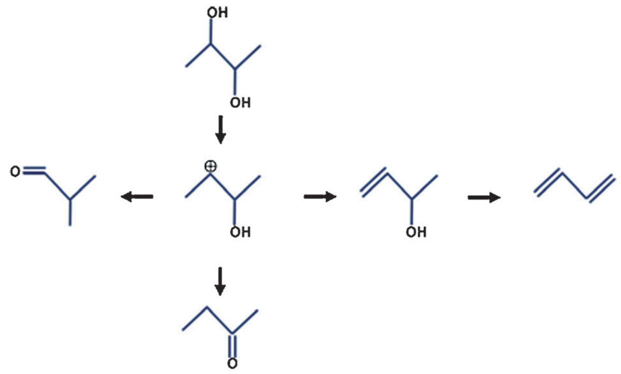


Figure 1. Catalytic activity of γ-Al_2O_3 as a function of flow rate.



Scheme 1. Methyl ethyl ketone, isobutyraldehyde and 1,3-butadiene derived in the dehydration of 2,3-butanedioldehydration.

The performance of γ-Al_2O_3 was also studied under the optimized reaction conditions (Figure 2 and Table 6). No activity of γ-Al_2O_3 was observed at 150 °C. At low temperatures (200–250 °C), IBA is the major product with lower production of BDE and BTO. Once the reaction temperature was increased to 300 °C, the selectivity to IBA decreased from 78% to 21%, whilst the conversion of BDO simultaneously increased from 2% to 8%. The catalytic performance of γ-Al_2O_3 was quite stable at reaction temperatures ranging from 300 to 350 °C, while no production of MEK was detected. However, at the higher temperature, production of MEK was observed and increased as a function of reaction temperature. It is suggested that production of IBA and MEK via the pinacol–pinacolone rearrangement may occur under different reaction conditions, with the latter product favored by higher reaction temperature. The results also suggested that the carbonium ion (Equation 2) formed via acid-catalyzed extraction of the OH group, might be the key intermediate for the generation of IBA, BTO, BDE, and MEK (Scheme 1). Strong acidity or higher temperatures favor the production of MEK due to either strong adsorption on the catalyst or instability of the intermediate at the higher temperature. Weaker adsorption assigned to moderate acidity and decreased re-adsorption could promote the stepwise elimination of hydroxyl groups, which improved the production of BDE.

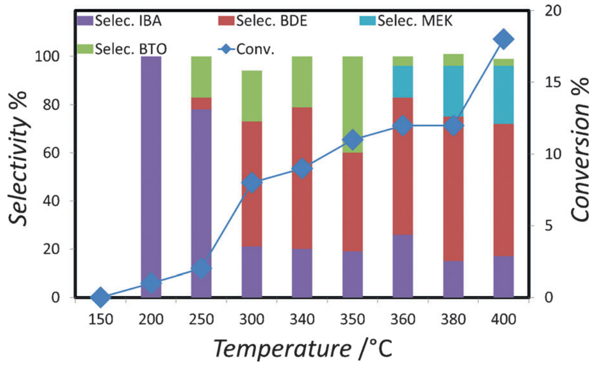


Figure 2. Catalytic activity of γ-Al_2O_3 as a function of reaction temperature.

Table 6. Catalytic performance of γ-Al_2O_3 catalysts at different temperatures.[a]

	Catalyst	Temp. [°C]	Conv. [%]	Selec. [%]					Carbon Balance [%]
				BDE	IBA	MEK	BTO	Enenol	
1	γ-Al_2O_3	150	0	–	–	–	–	–	
2		200	1	–	100	–	–	–	100
3		250	2	5	78	–	17	–	100
4		300	8	52	21	–	21	6	99
5		340	9	59	20	–	21	-	101
6		350	11	41	19	0	40	–	96
7		360	12	57	26	13	4	–	98
8		380	12	60	15	21	5	–	99
9		400	18	55	17	24	3	–	90[b]

[a] Reaction conditions: 10 wt% BDO, 0.02 mL min^{-1}, 3 mg catalysts, 300 mL min^{-1} Ar. [a] Mass production of propene.

Dehydration of 3-buten-2-ol by using γ-Al_2O_3 was tested under similar reaction conditions (10 wt% BTO in water, 0.02 mL min^{-1}, 3 mg catalysts, 300 mL min^{-1} Ar, Table 7) to those used previously for BDO. Almost complete transformation of BTO to BDE was observed with only a small amount of IBA being detected in the products. The production of IBA could be attributed to the rearrangement of 3-buten-2-ol or addition of water to BDE.

Table 7. Catalytic dehydration of 3-buten-2-ol.[a]

Catalyst	Temp. [°C]	Conv. [%]	Selec. %				Carbon Balance [%]
			BDE	IBA	MEK	Enenol	
γ-Al_2O_3	350	94	96	4	–	–	100

[a] Reaction conditions: 10 wt% 3-buten-2-ol in water, 0.02 mL min^{-1}, 3 mg catalysts, 300 mL min^{-1} Ar.

In this work, γ-Al_2O_3 has been confirmed as a catalyst for the direct dehydration of BDO to BDE, a valuable monomer for the production of synthetic rubber. By using trace amounts of catalyst and a high flow rate in a fixed bed reactor, 10% BDO conversion could be achieved with >80% selectivity to BDE and BTO. The presence of water efficiently improved the overall catalytic performance by reducing oligomerization of BDE.

Experimental Section

Catalysts, including α-Al_2O_3 (99.8% trace metal basis, N_2 BET surface area, 1 m^{2}g^{-1}) and γ-Al_2O_3 (99.8% trace metal basis, N_2 BET surface area, 105 m^{2}g^{-1}) were purchased from Sigma Aldrich and used as received, and silica tungstic acid was obtained from Johnson Matthey. Catalytic dehydration was conducted by using a laboratory fixed bed reactor equipped with a vaporizer. 2,3-Butanediol (BDO, 10 wt% aqueous solution) was pumped into the middle of the vaporizer with a flow rate of 0.02 mL min^{-1} where it was vaporized in a flow of argon carrier gas and fed to the catalyst. The temperature of the vaporizer was set to the same as the reaction temperature. All of the catalysts were pressed and sieved to a uniform particle size distribution of 600–800 μm before use and were packed into a 0.8 mm i.d. stainless steel reactor between plugs of quartz wool. Catalyst amounts ranged from 3–500 mg. A glass collection vessel filled with distilled water was connected to the end of the reactor, which was cooled with ice-water, and then gaseous products were collected in a gas bag.

For the first hour of the reaction the products were expelled through a vent and the product collection was started only from the second hour onwards to maximize the mass balance recovery of the products by giving enough time to achieve a proper balance of substrate/water vapor in the reactor. Then the reaction products were collected in cold traps filled with a known amount of distilled water. Two traps were used to ensure that any carryover from the first trap was collected in the subsequent trap (however, for most of the cases, no products were observed in the second trap). The gas phase was collected in a gas sampling bag and analyzed offline by gas chromatography. The contents of the traps were worked-up and also analyzed by gas chromatography.

The product work-up procedure and analysis were as follows. After addition of a known amount of propanol, as an internal standard to the traps, 0.75 mL aqueous solution were added to dichloromethane (1–2 mL), which was then dried over sodium sulfate. After filtration the samples were analyzed by using a Varian 430-GC gas chromatograph equipped with a capillary column (Restek, Stabilwax, id 0.25 mm × 15 m). Quantification was achieved through a calibration against five different concentrations of authentic samples using propanol as an internal standard, for all products. The injector and detector ports were maintained at 250 °C and the oven was programmed from 40 °C to 200 °C at a rate of 30 °C min^{-1} after 3 min waiting at the initial temperature of 40 °C. The column temperature was kept at 200 °C for an additional 2 min. Gas phase analysis was performed using the same gas chromatograph and column, applying a constant temperature program (35 °C) for 8 min. The peak of the BDE can be readily distinguished from propene. Quantification of BDE was achieved through a calibration against five different concentrations, made by controlling the flow rates of inert argon gas and BDE. Possible production of CO and CO_2 was analyzed by using a Varian 450-GC gas chromatograph equipped with FID & TCD detectors, a methanizer, and a CP-SiL5CB column (50 m, 0.33 mm diameter, He carrier gas). The qualitative production of the butadiene was also confirmed by GC-MS.

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Keywords: 1,3-butadiene · 2,3-butanediol · alumina · catalysis · dehydration

[1] What happened to biofuels? *The Economist*, September 7, **2013**, 18–12.
[2] P. Gallezot, *Chem. Soc. Rev.* **2012**, *41*, 1538–1558.
[3] C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon, M. Poliakoff, *Science* **2012**, *337*, 695–699.
[4] M.-J. Syu, *Appl. Microbiol. Biotechnol.* **2001**, *55*, 10–18.
[5] A. Shrivastav, J. W. Lee, H. Y. Kim, Y. R. Kim, *J. Microbiol. Biotechnol.* **2013**, *23*, 885–896.
[6] M. Dworkin, S. Falkow, *The Prokaryotes: Vol. 1: Symbiotic Associations, Biotechnology, Applied Microbiology*, Springer, Heidelberg, **2006**, pp. 723.
[7] M. E. Winfield, *J. Council Sci. Ind. Res.*, **1945**, *18*, 412–423; M. E. Winfield, *Aust. J. Sci. Res.* **1950**, 3, 290–305.
[8] U. V. Mentzela, M. S. Holm, *Appl. Catal. A* **2011**, *396*, 59–67.
[9] Q. Zheng, M. D. Wales, M. G. Heidlage, M. Rezac, H. Wang, S. H. Bossmann, K. L. Hohn, *J. Catal.* **2015**, *330*, 222–237.
[10] H. Duan, D. Sun, Y. Yamada, S. Sato, *Catal. Commun.* **2014**, *48*, 1–4.
[11] H. Duan, Y. Yamada, S. Sato, *Appl. Catal. A* **2015**, *491*, 163–169.
[12] W. Kim, W. Shin, K. J. Lee, H. Song, H. S. Kim, D. Seung, I. N. Filimonov, *Appl. Catal. A-Gen.*; **2016**, *511*, 156–167; **2016**, 511, 156–167
[13] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098.
[14] I. M. Atadashi, M. K. Aroua, *Renewable Energy* **2011**, *36*, 437–443.
[15] R. R. Emerson, M. C. Flickinger, G. T. Tsao, *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 473–477.
[16] M. H. Haider, N. F. Dummer, D. W. Knight, R. L. Jenkins, M. Howard, J. Moulijn, S. H. Taylor, G. J. Hutchings, *Nat. Chem.* **2015**, *7*, 1028–1032.
[17] Y. Mizuho, *A Study on Catalytic Conversion of Non-Food Biomass into Chemicals Fusion of Chemical Sciences and Engineering*, Springer, Heidelberg, 1st ed. **2016**, CH 1.2, pp. 21.

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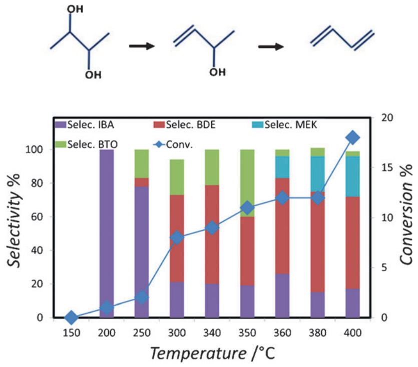
One-Step Production of 1,3-Butadiene from 2,3-Butanediol Dehydration



The direct production of 1,3-butadiene from the dehydration of 2,3-butandiol by using alumina as catalyst is reported. Under optimized kinetic reaction conditions, the production of methyl ethyl ketone and isobutyraldehyde, formed via the pinacol–pinacolone rearrangement, was markedly reduced and almost 80 % selectivity to 1,3-butadiene and 1,3-butadiene could be achieved. The amphoteric nature of γ-Al_2O_3 was identified as important and this contributed to the improved catalytic selectivity when compared with other acidic catalysts