



Short communication

Vapor-phase hydrogenation of acetoin and diacetyl into 2,3-butanediol over supported metal catalysts



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ABSTRACT

Vapor-phase catalytic production of 2,3-butanediol from acetoin and diacetyl was investigated over the supported metal catalysts such as Ni, Co, Cu, and Ag. A yield of 2,3-butanediol higher than 90% can be obtained from both acetoin and diacetyl over Ni/SiO₂ catalyst in an H₂ flow at 150 °C. Since the hydrogenation is an exothermic reaction, a low temperature is favorable to gain a full production of 2,3-butanediol. It was found that the equilibrium among 2,3-butanediol, acetoin, and diacetyl could be achieved at a contact time of the reactants with catalyst longer than 1.67 h. The pressure equilibrium constants in the hydrogenation were calculated by the outlet gas composition.

1. Introduction

2,3-Butanediol (2,3-BDO) is a promising platform chemical for its wide applications in synthetic rubbers [1–4], printing inks [5], perfumes [6], solvents, antifreeze agents [7], fuel, fuel additives [2,8], food stuffs [9], drugs [10], pharmaceuticals [11], moistening and softening agents [2] etc. The market demand of 2,3-BDO in 2018 is predicted as ca. 74 kt and is still growing annually at a rate of ca. 4–7% [12–14]. However, due to the instability of fossil resource prices and the costly chemical synthesis, 2,3-BDO is still extremely expensive (8000–18,000 USD/ton) [2,12]. Fortunately, the environmentally friendly bio-production of 2,3-BDO from biomass materials such as glucose, galactose, mannitol, arabinose, and xylose through fermentation has showed a great future for commercial opportunities. The technologies for 2,3-BDO formation from biomass have been highly developed and can be even dated back to the report in 1906 by Harden and Walpole [13]. However, the theoretical value (0.5 g/g) of 2,3-BDO yield from these biomass is very difficult to reach [13,15]. In fact, in the fermentation process, two pyruvates from glucose were condensed to an α -acetolactate, and then followed by releasing a CO₂ to form acetoin (3-hydroxy-2-butanone, AC). Meanwhile, under oxygen supply conditions, α -acetolactate is readily to be decarboxylated into diacetyl (2,3-butanedione, DA). During the fermentation, the two intermediates, especially AC, always co-exist with 2,3-BDO as the main products [16,17]. Besides, separation of those intermediate products for a high purity of 2,3-BDO is still complex and costly. In addition, even with a little amount, DA can cause some health problems especially in the respiratory system [18]. Therefore, further study on the conversion of

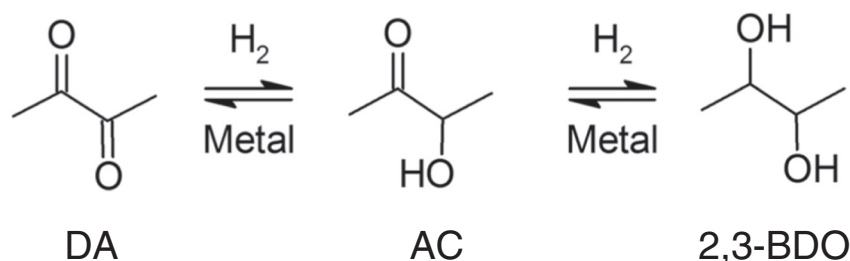
AC and DA into 2,3-BDO is needed.

As to the further hydrogenation of AC and DA into 2,3-BDO, the fermentation and enzymatic reactions processes have been studied. Both AC and DA can be reduced into 2,3-BDO with the corresponding acetoin/diacetyl reductase. Both AC and 2,3-BDO can be produced from DA and then AC can be also hydrogenated into 2,3-BDO [19,20]. However, sorting and preparing the efficient strain is costly for the industrial production at a large scale. Only a few reports were found on the liquid-phase hydrogenation of DA via the catalytic chemical processes, while they are target on chiral syntheses of 2,3-BDO. These catalytic chemical processes seem suitable for industrial production at a large scale but costly for the necessity of solvent, the usage of precious metals, such as Ru [21,22], Pt [21–25], Rh [21,26], Pd [21,27,28], Ir, and Os [21], a long reaction time, and high pressure conditions. The catalytic performances of several catalysts on the hydrogenation of DA [21,24,26] are summarized in Table S1 of supplementary information. In contrast, the hydrogenation of AC is rarely studied: 100% yield of 2,3-BDO is achieved by Pt/Al₂O₃ catalyst in ethanol at 60 °C and 400 atm [24].

In this paper, we examined the vapor-phase catalytic hydrogenation of AC as well as DA over several catalysts with the supported base metals such as Ni, Co, Cu, and Ag to produce 2,3-BDO at an atmospheric pressure of H₂. Vapor-phase catalytic hydrogenation for fine chemical synthesis is convenient to separate and environment friendly for the absence of solvent, and the supported metal catalysts are easily prepared via the incipient wetness impregnation. The interconversion of AC, DA and 2,3-BDO was also studied to understand the equilibrium and their equilibrium values.

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2. Experimental

2.1. Catalyst samples

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and AgNO_3 used as the metal sources were purchased from Wako Pure Chemical Industry Ltd. Japan. The supports such as ZrO_2 (JRC-ZRO-4, specific surface area, $\text{SA} = 29.8 \text{ m}^2/\text{g}$) and MgO (JRC-MGO-3 1000A, $\text{SA} = \text{ca. } 16 \text{ m}^2/\text{g}$) were supplied by the Reference Catalyst Division (former Committee), the Catalysis Society of Japan. SiO_2 (Q-10, $\text{SA} = 259 \text{ m}^2/\text{g}$) was supplied by Fuji Silysia Chemical Ltd. Japan, ZnO ($\text{SA} = 25.6 \text{ m}^2/\text{g}$) was purchased from Kanto Chemical Co. Inc. Japan, and $\text{SiO}_2\text{-Al}_2\text{O}_3$ (N631L, Al_2O_3 content 15 wt%, $\text{SA} = 440 \text{ m}^2/\text{g}$) was purchased from Nikki Chemical Co., Ltd. Activated carbon (A-BAC-LP, $\text{SA} = 1100\text{--}1300 \text{ m}^2/\text{g}$) was supplied by Kureha Co., Ltd. Japan.

In this study, all the reagents were used as received without further pretreatment. Each aqueous solution of the corresponding nitrate with the prescribed amount of metal was impregnated onto the supports by incipient wetness impregnation, respectively. The resulting samples were dried at 110°C for 12 h, and then calcined in air at a prescribed temperature for 3 h to obtain the supported metal oxide catalysts. The supported metals are expressed as x-M/support, where x is the molar percentage of the metal (calculated as $100 \text{ M} / (\text{M} + \text{support})$) and M represents the loaded metal.

2.2. Catalytic reactions and characterization

Prior to the reaction, a catalyst sample (0.038–2.0 g) was preheated and reduced in a fixed bed flow reactor in an H_2 flow at a prescribed temperature for 1 h, then the reactor was cooled to the reaction temperatures ($110\text{--}250^\circ\text{C}$). The reactant was fed into the reactor at a liquid flow rate of 1.2 g h^{-1} together with an H_2 flow rate of $80 \text{ cm}^3 \text{ min}^{-1}$ at 12°C ($\text{H}_2/\text{AC} = 16.4$). The liquid effluent collected

periodically was analyzed by gas chromatography (FID-GC-8A, Shimadzu, Japan) with a 60-m capillary column (InertCapWAX-HT). The products were identified by gas chromatography with a mass spectrometer (GCMS-QP5050A, Shimadzu, Japan) with a 30-m capillary column (DB-WAX). The catalytic activity was evaluated by averaging the conversion and selectivity data in the initial 3 h. Conversions of AC, DA and 2,3-BDO, and the selectivities to their corresponding products were defined as mol%. During the catalytic reactions, products and unreacted reactant were recovered with carbon balance higher than 95%.

To determine the suitable reduction temperatures of the metal oxides, the temperature-programmed reduction (TPR) measurements were investigated. A sample was filled in the central part of a quartz tube. A mixture of H_2 and N_2 gases ($\text{H}_2/\text{N}_2 = 1/9$) was flowed into the quartz tube with a flow rate of $10 \text{ cm}^3 \text{ min}^{-1}$ at ambient pressure. The amount of H_2 consumed for the sample reduction was monitored by the thermal conductivity detector (TCD). After the baseline of TCD signal had kept stable for 2 h, the sample was heated from room temperature to 900°C at a heating rate of 5°C min^{-1} . The most suitable reduction temperature was determined as the point, at which the H_2 consumption was completed.

The thermo-gravimetry differential thermal analysis (TG-DTA, Thermoplus 8120E2, Rigaku, Japan) was also performed to determine the decomposition temperatures of either nitrates or coke deposited on the surface of the used catalysts. $\alpha\text{-Al}_2\text{O}_3$ (10.0 mg) was used as the reference and the sample weight was 10–15 mg. The temperature increasing rate was 5°C min^{-1} from room temperature to 900°C .

3. Results and discussion

3.1. Hydrogenation of AC over various supported metal catalysts

We investigated several typical metal catalysts such as Ni, Ag, Co and Cu for the hydrogenation of AC. Since the decomposition of all these corresponding nitrates completed below 300°C (TG-DTA profiles not shown), all the dried precursors were calcined at 300°C after

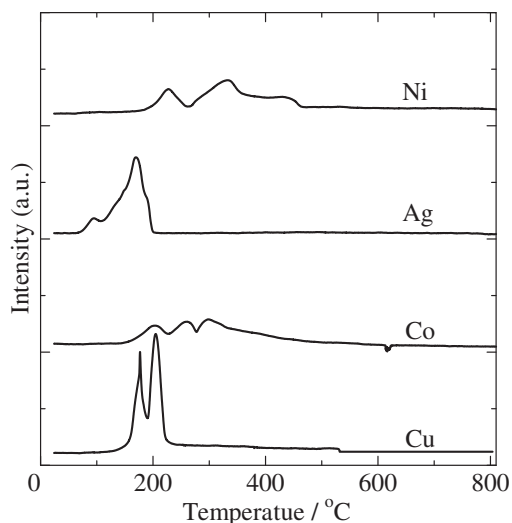


Fig. 1. TPR profiles for Ni, Ag, Co and Cu catalysts supported on ZrO_2 (6.7-M/ ZrO_2).

Table 1
Hydrogenation of AC over several metal catalysts supported on ZrO_2 (6.7-M/ ZrO_2) at 200°C .

Metal M	Conversion (mol%)	Selectivity (mol%)			Yield (mol%)	
		2,3-BDO	DA	Others	2,3-BDO	DA
Ni ^a	64.4	81.3	5.8	12.9 ^c	52.4	3.7
Co ^a	92.9	14.0	38.0	48.0 ^d	13.0	35.7
Cu ^b	62.2	99.9	0.1	0.0	62.1	6.2
Ag ^b	8.5	36.2	10.2	53.6	0.8	3.2

W/F = 0.42 h (except Ag/ ZrO_2 , W/F = 0.83 h), the flow rate of H_2 carrier gas was $80 \text{ cm}^3 \text{ min}^{-1}$ and the conversion and selectivity were calculated as the average for the initial 3 h.

^a Reduced at 400°C for 1 h.

^b Reduced at 250°C for 1 h.

^c Included 2-butanol 5.8%, ethanol 4.7%.

^d Included 2-butanol 29.4%.

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