



# Dual-bed catalytic system comprising $\text{Al}_2\text{O}_3$ and $\text{Ba}/\text{Al}_2\text{O}_3$ with enhanced 1-octene productivity in 1-octanol dehydration for linear $\alpha$ -olefin production

Young-eun Kim<sup>a,c</sup>, Unho Jung<sup>a</sup>, Dahye Song<sup>a</sup>, Hyo Been Im<sup>a</sup>, Tae Ho Lee<sup>a</sup>, Dong Hyun Chun<sup>b</sup>, Min Hye Youn<sup>b</sup>, Ki Bong Lee<sup>c,\*</sup>, Kee Young Koo<sup>a,d,\*</sup>

<sup>a</sup> Hydrogen Research Department, Korea Institute of Energy Research (KIER), 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea

<sup>b</sup> Carbon Conversion Research Laboratory, Korea Institute of Energy Research (KIER), 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea

<sup>c</sup> Department of Chemical & Biological Engineering, Korea University, 1 Anam-Dong, Seongbuk-Gu, Seoul 02841, Republic of Korea

<sup>d</sup> Advanced Energy and System Engineering, University of Science and Technology (UST), 217 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea

## ARTICLE INFO

### Article history:

Received 27 April 2022

Revised 16 November 2022

Accepted 20 November 2022

Available online 25 November 2022

### Keywords:

Linear  $\alpha$ -olefin

Dual-bed system

1-Octene

Alcohol dehydration

Barium impregnation

Aluminum oxide catalyst

## ABSTRACT

To produce high-purity 1-octene, the dehydration of 1-octanol was performed over a dual-bed catalytic system comprising  $\text{Al}_2\text{O}_3$  and  $\text{Ba}/\text{Al}_2\text{O}_3$  catalysts. The influence of the catalyst weight on the activities of  $\text{Al}_2\text{O}_3$  and  $\text{Ba}/\text{Al}_2\text{O}_3$  single-bed systems was initially investigated at liquid hourly space velocities (LHSV) of 7–168  $\text{h}^{-1}$  at 400 °C. For the  $\text{Al}_2\text{O}_3$  single-bed system, the 1-octene selectivity decreased with an increase in the catalyst weight. Although the 1-octene selectivity of  $\text{Ba}/\text{Al}_2\text{O}_3$  increased owing to the anti-Saytzeff effect, its yield was limited due to a low 1-octanol conversion. The efficiency of the dual-bed catalytic system was subsequently investigated by varying the catalyst bed ratio (i.e.,  $x\text{Al}-y\text{Ba}$ ). The 40Al-60Ba catalytic system afforded a higher conversion (95.3%) and productivity than the  $\text{Ba}/\text{Al}_2\text{O}_3$  single-bed system at an LHSV of 56  $\text{h}^{-1}$ . Moreover, the 10Al-90Ba catalytic system with a high  $\text{Ba}/\text{Al}_2\text{O}_3$  catalyst ratio exhibited a high 1-octene productivity at LHSVs of 7–28  $\text{h}^{-1}$ , while also yielding a high-purity product. The single-bed system exhibited a lower selectivity toward 1-octene than the dual-bed system, and after 100 h, the 10Al-90Ba dual-bed system offered a stable catalytic performance regardless of the small reductions in the 1-octene selectivity and yield.

© 2022 The Authors. Published by Elsevier B.V. on behalf of The Korean Society of Industrial and Engineering Chemistry. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

## Introduction

Linear  $\alpha$ -olefins (LAOs), which possess a linear carbon chain with a terminal double bond, are used to produce various chemicals such as linear low-density polyethylene (LLDPE), synthetic lubricants, plasticizer alcohols, drilling fluids, and surfactants. More specifically, >50% of the globally produced LAOs are used

for the production of polyethylene [1–3]. In addition, 1-butene, 1-hexene, and 1-octene, which are co-monomers of LLDPE, occupy the largest market share in the LAO sector [4]. However, increasing the length of the carbon chain reduces the production volume and increases the associated costs, and hence, the demand for 1-butene, 1-hexene, and 1-octene is high [5]. Moreover, the tensile strengths and thermal stability of LLDPEs improve upon increasing the carbon chain length of the co-monomer [6]. Furthermore, when blended with polypropylene and LLDPE, an ethylene-octene copolymer is used as both an elastomer [7,8] and a rubber [9]; consequently, the demand for 1-octene is expected to steadily increase in the near future [5].

1-Octene is mainly produced by a full-range method based on the oligomerization of ethylene, which results in the production of olefins and isomers with varying carbon chain lengths, thereby complicating the separation process. For example, leading LAO manufacturers, such as Shell, BP Amoco, and Chevron Phillips, carry out this ethylene oligomerization process under high pressure conditions (0.5–19 MPa) using homogeneous catalysts (e.g., Ni-

**Abbreviations:** BET, Brunauer-Emmett-Teller; BJH, Barrett-Joyner-Halenda; DOE, dioctyl ether; DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy; ICP-OES, inductively coupled plasma optical emission spectroscopy; LAO, linear  $\alpha$ -olefin; LAS, Lewis acid site;  $L_{\text{cat}}$ , length of catalyst bed; LHSV, liquid hourly space velocity; LLDPE, linear low-density polyethylene;  $T_{\text{cat}}$ , temperature of catalyst bed; TGA, thermogravimetry analysis; TOS, time on stream; TPD, temperature-programmed desorption;  $W_{\text{cat}}$ , catalyst weight; XRD, X-ray diffraction.

\* Corresponding authors at: Hydrogen Research Department, Korea Institute of Energy Research (KIER), 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea (K.Y. Koo); Department of Chemical & Biological Engineering, Korea University, 1 Anam-Dong, Seongbuk-Gu, Seoul 02841, Republic of Korea (K.B. Lee).

E-mail addresses: [kibonglee@korea.ac.kr](mailto:kibonglee@korea.ac.kr) (K.B. Lee), [kykoo@kier.re.kr](mailto:kykoo@kier.re.kr) (K.Y. Koo).

<https://doi.org/10.1016/j.jiec.2022.11.060>

1226-086X/© 2022 The Authors. Published by Elsevier B.V. on behalf of The Korean Society of Industrial and Engineering Chemistry.

This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

complexes and Al–organic compounds) [10,11]. However, the oligomerization of ethylene simultaneously produces C2–C30 olefins, which require complicated separation processes to produce the highly demanded C4–C8 olefins. Thus, and an on-purpose LAO process with a high selectivity is required to achieve this goal. Thus, research on the on-purpose method, which increases the economic efficiency by enhancing the selectivity of C4–C8 olefin, has recently attracted attention [2,12,13]. Various on-purpose processes were suggested for 1-octene production such as enhanced ethylene oligomerization (i.e., ethylene tri- and tetramerization), butadiene dimerization, and the 1-heptene upgrading process proposed by Sasol [4]. More specifically, this 1-heptene upgrading process involves the hydroformylation of 1-heptene, subsequent hydrogenation to 1-octanol, and a dehydration of 1-octanol to produce a C8 alkene, C16 dioctyl ether (DOE), and water [14,15]. The water and DOE components can be easily separated because of the large differences in their boiling points compared to that of 1-octene. However, the physical properties of the *cis*- (i.e., *cis*-2-octene) and *trans*-isomers of octene (i.e., *trans*-2-octene, *trans*-3-octene, and *trans*-4-octene) are similar to those of 1-octene, which complicates the subsequent separation process. To resolve this problem, the dehydration of 1-octanol is performed at a low conversion rate (<20%) wherein few isomers are produced [16].

To date, several studies have investigated the mechanism of isomer formation during alcohol dehydration. Primary alcohol dehydration leads to the generation of double-bond isomers via the hydration–dehydration of 1-olefin that is re-adsorbed onto the acidic sites of the catalyst [17,18]. In addition, Dabbagh et al. [19] studied the catalytic activities of metal oxide catalysts such as  $\text{WO}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ThO}_2$ ,  $\text{In}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  in the dehydration of secondary alcohols. The selectivities of such systems toward 1-alkene and *cis*-2-alkene, which have low thermodynamic stabilities, were found to be higher than those for the thermodynamically stable *trans*-2-alkene. This can be attributed to the fact that the selectivity of the system depends on the electron density of the metal oxide surface, wherein a catalyst with a high basicity exhibited a high 1-alkene selectivity. Studies into the temperature-programmed desorption (TPD) of 1-butanol [20] yielded similar results. Furthermore, when the acid–base properties of the  $\gamma\text{-Al}_2\text{O}_3$  catalyst were modified upon the addition of F or Na, the Na-containing  $\text{Al}_2\text{O}_3$  catalyst exhibited more basic properties and a higher 1-butene selectivity with a reduced desorption of hydrocarbons. According to our previous report [21,22], when Ba, an alkaline earth metal, was impregnated onto the surface of the  $\text{Al}_2\text{O}_3$  catalyst, the 1-alkene selectivity of the catalyst improved with increasing Ba content owing to the inductive effect. This was attributed to the fact that Ba impregnation reduced number of the strong Lewis acid sites (LAS) present on the  $\text{Al}_2\text{O}_3$  catalyst, consequently suppressing the re-adsorption of 1-octene by inducing the anti-Saytzeff effect. Despite the improvement in the 1-alkene selectivity (38.8%) owing to the increased basicity of the 1.5 wt% Ba/ $\text{Al}_2\text{O}_3$  catalyst, the 1-alkene yield was limited because of the reduced alcohol conversion (22.1%) at 400 °C and a liquid hourly space velocity (LHSV) of 56 h<sup>−1</sup> [21].

Owing to the limitations of single-bed catalytic systems, they have been replaced with dual-bed catalytic systems. In many industrial processes, multiple catalyst types are loaded in the same reactor, sometimes even in the same catalyst bed. In the diesel or naphtha cracking process, the placement of a Ni–Mo catalyst on top of the Co–Mo catalyst during the hydrotreating process results in a greater reduction in the sulfur concentration was achieved [23]. In the case of the catalytic converters used for automobile off-gas, the use of a Rh catalyst bed under a Pt or Pd bed oxidized the unburned hydrocarbons, and as a result, the  $\text{NO}_x$  emissions were controlled [24]. In addition, during the oligomerization of ethylene, which is an exothermic reaction, a multiple fixed-bed catalytic system was used to maintain the reaction activity by controlling the

reaction temperature over each catalyst layer [25]. According to Morni et al. [26], the product selectivities of dual-bed catalytic systems (commonly consisting of zeolites, NiO, and  $\text{MoO}_3$ ) in the catalytic fast co-pyrolysis process were affected by the stacking order and mixing type. Such dual-bed systems comprising metal oxides and zeolite catalysts tend to possess higher aromatic selectivities than mixing systems. In this context, Tsai et al. [27] reported that greater quantities of pure benzene can be obtained when a dual-bed catalyst comprising an H-beta zeolite catalyst loaded at the end of a Pt/ZSM-12 catalyst is employed for the selective cracking of naphthene during alkylbenzene transalkylation. Furthermore, a catalyst affording a high product selectivity can be loaded along with a catalyst providing a higher conversion. According to Zeng et al. [28], the catalytic dehydration of 2,3-butanediol over a  $\text{Sc}_2\text{O}_3$  catalyst can change the acid–base properties of the catalyst, thereby altering the distribution of the product. Although an increase in the basicity of the secondary bed catalyst enhances the selectivity toward  $\alpha$ -olefins, in the presence of a strongly basic catalyst, side reactions such as dehydrogenation and conversion reduction processes can occur. In our previous studies [21], it was found that an  $\text{Al}_2\text{O}_3$  catalyst with acidic properties exhibited a high activity toward the alcohol dehydration reaction; however, its 1-octene selectivity decreased owing to the side reaction of hydration–dehydration. In addition, the Ba/ $\text{Al}_2\text{O}_3$  basic catalyst exhibits a high selectivity for the anti-Saytzeff elimination despite its low single-pass conversion during the alcohol dehydration process.

Thus, to counter this trade-off in the dehydration of 1-octanol, a dual-bed catalyst system is proposed, wherein a highly active  $\text{Al}_2\text{O}_3$  catalyst is placed on top of a Ba/ $\text{Al}_2\text{O}_3$  catalyst that displays a higher selectivity for the anti-Saytzeff elimination. This method is expected to prevent the hydration–dehydration side reaction taking place to afford a high single-pass conversion. Furthermore, the Al/Ba ratio under different LHSVs is optimized.

## Material and methods

### Preparation

The  $\text{Al}_2\text{O}_3$  catalyst (spherical particles, diameter 1 mm) was obtained from Sasol (Germany), and was calcined at 500 °C at a rate of 5 °C/min for 6 h under air before use.  $\text{Al}_2\text{O}_3$  impregnated with 1.5 wt% Ba was prepared using the incipient wetness method.  $\text{Ba}(\text{NO}_3)_2$  (ACS reagent grade, Sigma-Aldrich) was used as the precursor, and was dissolved in water at 80 °C over 30 min. The solution was then added to the pre-calcined  $\text{Al}_2\text{O}_3$ , and was further calcined at 500 °C under air for 4 h.

### Catalyst characterization

The Ba content of each catalyst was confirmed using inductively coupled plasma optical emission spectroscopy (ICP-OES). The catalysts were pretreated using a microwave (Anton Paar Multiwave PRO) in an acidic solvent (35% HCl 7 mL + 70%  $\text{HNO}_3$  3 mL). The physical properties of the catalysts were then determined using the X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), and Barrett–Joyner–Halenda (BJH) techniques. BET–BJH analyses were performed to calculate the surface areas of the catalysts using a BELSORP-max instrument (BEL Japan, Inc.) at −196 °C. The crystallographic structures of the catalysts were determined by XRD using a D/Max-2500 v/PC diffractometer (Rigaku). The acid–base properties of the catalyst were confirmed by conducting Fourier transform infrared (FTIR) spectroscopic analysis using a Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific) equipped with a praying mantis DRIFTS diffuse reflectance attachment (Harrick).  $\text{CO}_2$  and pyridine were used as the probe gases for basicity and

acidity, respectively. After pretreating the sample at 400 °C in 5 vol O<sub>2</sub>/He, the sample was exposed to the probe gas at 100 °C for 30 min. The sample was then purged under a He flow for 1 h. The data were scanned at 4 cm<sup>-1</sup> and are reported as averages over 128 scans. The basicity of the catalyst was investigated by CO<sub>2</sub>-temperature programmed desorption using BELCAT-B instrument (BEL Japan, Inc.) equipped with a thermal conductivity detector (TCD). The sample was loaded in a quartz tube (50 mg), pretreated according to the same process employed for the FTIR samples, and cooled to 50 °C. CO<sub>2</sub> adsorption was performed at 50 °C for 30 min in 10 vol.% CO<sub>2</sub>/He, and after this time, the weakly adsorbed CO<sub>2</sub> was purged with a He carrier gas. Subsequently, the sample was heated from 50 to 500 °C at a rate of 5 °C/min under He gas. The characteristics of the catalysts determined by XRD and CO<sub>2</sub>-TPD were presented in a previous report [21]. Moreover, coke formation was investigated by Raman spectroscopy (LabRAM HR Evolution Visible NIR, HORIBA) in the range of 500–2000 cm<sup>-1</sup> and with a 514 nm laser source. Thermogravimetric analysis (TGA, TGA2, Mettler Toledo) was also performed to quantitatively analyze the degree of coke formation. More specifically, the used catalysts (30 mg) were oxidized by heating from 30 °C to 800 °C at a heating rate 10 °C/min under air. The degree of coke formation was determined using the equation provided in the [Supporting Information](#).

### Catalytic experiments

A quartz reactor (9.5 mm) in a fixed-bed reactor system was used for the 1-octanol dehydration reaction. The Al<sub>2</sub>O<sub>3</sub> catalyst was stacked on the upper site of the 1.5 wt% Ba/Al<sub>2</sub>O<sub>3</sub> layer. For the vaporization and distribution of 1-octanol, 1 mm of SiC (Goodfellow Corp.) per 1.0 g of catalyst was added to the top and bottom of the catalyst bed layer. A flow diagram of the reaction system and details regarding the catalyst bed are provided in [Fig. 1](#), wherein the length of the catalyst bed ( $L_{cat}$ ) was within the range of 0.7–2.1 cm (catalyst loading weight,  $W_{cat}$  = 0.2–0.6 g). The volume and density of the packed catalysts were 0.74 mL and 0.81 g·mL<sup>-1</sup>, respectively. The dual-bed systems were denoted as xAl-yBa, where x and y are the volume ratios of Al<sub>2</sub>O<sub>3</sub> and Ba/Al<sub>2</sub>O<sub>3</sub>, respectively. The catalyst bed was heated to 400 °C at the rate of 5 °C·min<sup>-1</sup> under a N<sub>2</sub> flow (50 mL·min<sup>-1</sup>), and was maintained at this temperature for 1 h using a thermocouple placed at the center of the bed. After turning off the N<sub>2</sub> gas flow, the 1-octanol gas preheated to 300 °C was infused into the catalyst bed using a high-performance liquid chromatography pump (NP-KX-201, NS). The reaction tests were performed at LHSVs of 7–168 h<sup>-1</sup> (weight hourly space velocity (WHSV): 7–172 h<sup>-1</sup>) for 2 h at atmospheric pressure. The catalytic test was performed at 400 °C with an LHSV of 21 h<sup>-1</sup> for a time-on-stream (TOS) of 100 h. Gas chromatography–flame ionization detection (7980-B, Agilent) was carried out using an HP-5 column (19091 J-413, Agilent) to analyze the following organic compounds: 1-octanol, 1-octene, *cis*-2-octene, *trans*-2-octene, *trans*-3-octene, *trans*-4-octene, and DOE. No other octene double-bond isomers, such as *cis*-3-octene and *cis*-4-octene, were observed through GC-FID and detailed hydrocarbon analysis (DHA, DHA ASTM D6730 system) ([Fig. S1](#)). The catalytic activity was calculated using the equations presented in the [Supporting Information](#).

## Results and discussion

### Characterization

The properties of the Al<sub>2</sub>O<sub>3</sub> and Ba-impregnated Al<sub>2</sub>O<sub>3</sub> catalysts are summarized in [Table 1](#). Although it was confirmed through ICP analysis that Ba/Al<sub>2</sub>O<sub>3</sub> was impregnated with approximately 1.5 wt % Ba, the XRD results ([Fig. S2\(a\)](#)) did not show any change in the

crystal phase caused by the impregnation of Ba. In addition, the BET ([Fig. S3\(b\)](#)) and BJH ([Fig. S3\(c\)](#)) results showed that only slight changes in the pore properties of the catalyst were observed following Ba impregnation; further, the properties were generally similar to those of the Al<sub>2</sub>O<sub>3</sub> catalyst without any impregnation.

As shown by the pyridine-FTIR results ([Fig. S3\(a\)](#)), the strong LAS peak (1621 cm<sup>-1</sup>) observed for the Al<sub>2</sub>O<sub>3</sub> catalyst weakened following Ba impregnation. In this context, previous studies have indicated that the intensity of the LAS peak is correlated with 1-octanol conversion because the LASs act as active sites in the dehydration of 1-octanol [21,22,29,30]. However, according to the anti-Saytzeff effect, the selectivity and purity of 1-octene should be affected by the basic properties of the catalyst. Therefore, the Lewis basic sites of the Al<sub>2</sub>O<sub>3</sub> and Ba/Al<sub>2</sub>O<sub>3</sub> catalysts were also investigated using CO<sub>2</sub>-FTIR spectroscopy ([Fig. S3\(b\)](#)). Consequently, a few peaks corresponding to CO<sub>2</sub> were observed for Al<sub>2</sub>O<sub>3</sub> because the Al<sup>3+</sup> ions, which act as LASs, were exposed on the Al<sub>2</sub>O<sub>3</sub> surface. Moreover, LAS peaks were detected at 1606, 1573, and 1362 cm<sup>-1</sup> for the Ba/Al<sub>2</sub>O<sub>3</sub> catalyst. The CO<sub>2</sub>-FTIR peak depends on the bond type between CO<sub>2</sub> and the basic oxygen atoms present on the catalytic surface [31,32]. For unidentate carbonate where CO<sub>2</sub> binds to the strong basic oxygen ion on the catalyst surface, CO<sub>2</sub> peaks arise due to symmetric and asymmetric O—C—O stretching vibrations (i.e., 1360–1400 and 1510–1560 cm<sup>-1</sup>, respectively) [33]. In addition, bidentate carbonate takes the form of CO<sub>2</sub> molecules bound to the medium-strength basic sites that originate from the metal species. These bidentate carbonate species exhibit two types of vibration modes, namely symmetric and asymmetric O—C—O stretching vibrations (i.e., at 1320–1340 and 1610–1630 cm<sup>-1</sup>, respectively). A similar trend was observed in the CO<sub>2</sub>-TPD analysis of CO<sub>2</sub> desorption ([Table 1](#)), wherein the Ba/Al<sub>2</sub>O<sub>3</sub> catalyst with a high Lewis basicity exhibited a higher CO<sub>2</sub> desorption amount (0.049 molCO<sub>2</sub>/g<sub>cat</sub>) than that of Al<sub>2</sub>O<sub>3</sub> (0.036 molCO<sub>2</sub>/g<sub>cat</sub>). From the aforementioned results, it was confirmed that the addition of 1.5 wt% Ba to the Al<sub>2</sub>O<sub>3</sub> catalyst influenced the acid–base properties of the catalyst surface, although few changes were observed in terms of the textural properties, BET surface area, and crystal phase. Thus, the effect of the catalyst acid–base properties on the catalytic activity in the dehydration of 1-octanol was then investigated along with the effectiveness of the dual-bed catalytic system.

### Application of the dual catalytic bed in the dehydration of 1-octanol

To confirm that the catalytic activity was affected by variation of the catalyst mass/bed length in a single-bed catalytic system, the effect of the catalyst weight/bed length was investigated by adjusting the LHSV (7–169 h<sup>-1</sup>) and the catalyst loading (0.2–0.6 g) at a reaction temperature of 400 °C. As shown in [Figs. S4 and S5](#), no change in the alcohol conversion was observed upon varying the catalyst mass/bed length; however, the 1-octene selectivity exhibited slight changes. More specifically, at an LHSV of 56 h<sup>-1</sup>, the 1-octene selectivity of the Al<sub>2</sub>O<sub>3</sub> catalyst with highly acidic properties decreased from 48.8% (0.2 g) to 46.7% (0.3 g) and 38.0% (0.6 g) upon increasing of the catalyst mass/bed length. On the other hand, the 1-octene selectivity of the highly basic Ba/Al<sub>2</sub>O<sub>3</sub> catalyst increased from 76.6% (0.2 g) to 77.6% (0.3 g) and 81.3% (0.6 g) at LHSV 56 h<sup>-1</sup>, due to the anti-Saytzeff effect. From these results, it was confirmed that a basic catalyst inhibits formation of the double bond isomer during the alcohol dehydration [35,36]. Thus, the two catalysts with opposite catalytic activities were applied in the dual-bed catalytic system; it should be noted that in such a system, it is necessary to optimize the catalyst weight/bed length of both catalysts to achieve a high 1-octene yield.

The catalytic activity of the dual-bed catalytic system was investigated for the dehydration of 1-octanol by varying the cata-

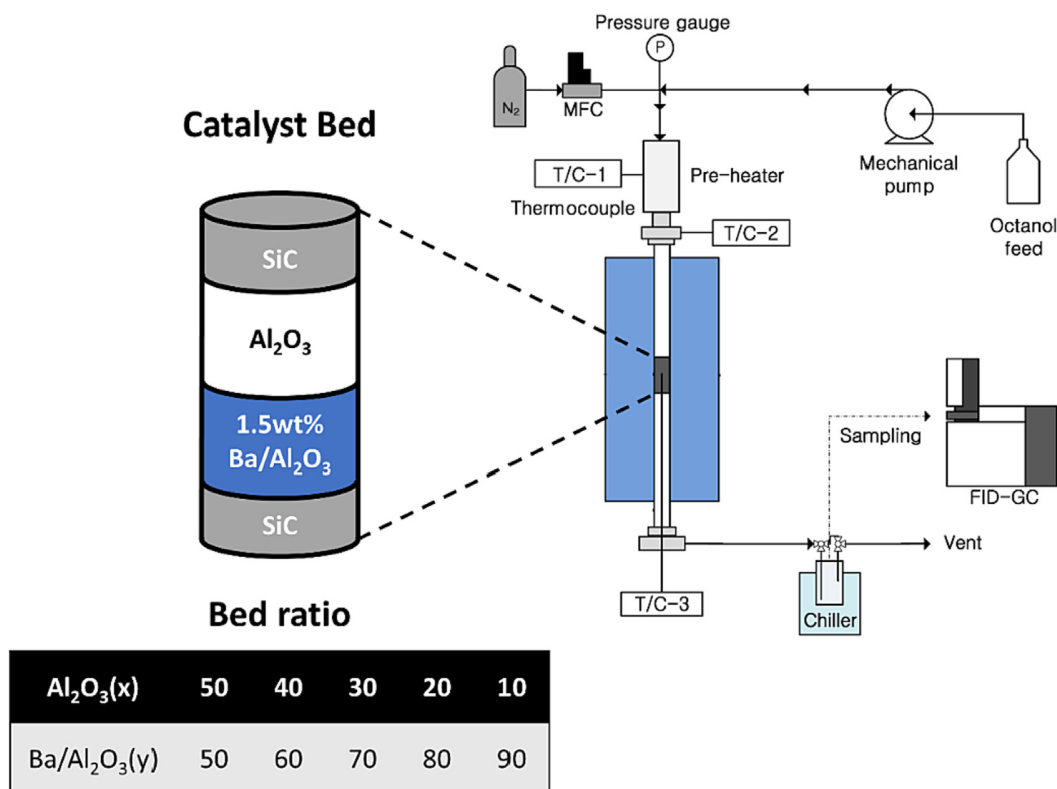


Fig. 1. Schematic outline of the 1-octanol dehydration reaction system and the dual-bed system.

Table 1

Summary of the characterization results for Al<sub>2</sub>O<sub>3</sub> and Ba/Al<sub>2</sub>O<sub>3</sub>.

| Catalyst                          | Ba content <sup>a</sup><br>(wt%) | Surface area <sup>b</sup><br>(m <sup>2</sup> /g) | Peak diameter <sup>b</sup><br>(nm) | Total pore volume <sup>b</sup><br>(cm <sup>3</sup> /g) | Desorption amount of CO <sub>2</sub> <sup>c</sup><br>(mmol/g) |
|-----------------------------------|----------------------------------|--------------------------------------------------|------------------------------------|--------------------------------------------------------|---------------------------------------------------------------|
| Al <sub>2</sub> O <sub>3</sub>    | –                                | 163.50                                           | 12.05                              | 0.4897                                                 | 0.036                                                         |
| Ba/Al <sub>2</sub> O <sub>3</sub> | 1.54                             | 159.61                                           | 12.05                              | 0.4787                                                 | 0.049                                                         |

<sup>a</sup> Confirmed by ICP-MS.

<sup>b</sup> Estimated from N<sub>2</sub> adsorption at –196 °C.

<sup>c</sup> Estimated from the integration of CO<sub>2</sub>-TPD peak [21].

lyst bed ratio (xAl–yBa) of the Al<sub>2</sub>O<sub>3</sub> and the Ba/Al<sub>2</sub>O<sub>3</sub> catalyst to maintains a high 1-octanol conversion at a high LHSV and inhibits isomer formation. For this purpose, a catalyst weight of 0.6 g was selected due to the fact that isomer formation in the Al<sub>2</sub>O<sub>3</sub> single catalytic bed occurred most actively when this catalyst weight was employed. Accordingly, the 50Al–50Ba system was initially examined wherein both catalyst layers had weights of 0.3 g to give a total catalyst weight of 0.6 g (Table 2). In the case of the 50Ba–50Al system in which the Al<sub>2</sub>O<sub>3</sub> and the Ba/Al<sub>2</sub>O<sub>3</sub> catalysts were stacked in a manner opposite to that of 50Al–50Ba, the 1-octene selectivity, yield, and purity were higher than those afforded over the single catalyst system. In addition, the 50Ba–50Al system had a lower selectivity (43.4%) than the 50Al–50Ba system (55.9%) at an LHSV of 21 h<sup>–1</sup> (Fig. S6). As mentioned above, the Al<sub>2</sub>O<sub>3</sub> catalyst layer (0.3 g) maintained a high conversion even at an LHSV of 56 h<sup>–1</sup> owing to the greater number of LASS; however, the 1-octanol conversion of the Ba/Al<sub>2</sub>O<sub>3</sub> catalyst rapidly declined from an LHSV of 28 h<sup>–1</sup>. As confirmed from the experimental results obtained for a Ba/Al<sub>2</sub>O<sub>3</sub> single catalytic bed (Fig. S5), the addition of Ba enhanced the 1-octene selectivity over long residence time with a low LHSVs (<56 h<sup>–1</sup>). Moreover, the 50Al–50Ba catalyst showed little reduction in the 1-octanol conversion even at a high

space velocity, similar to the case of the Al<sub>2</sub>O<sub>3</sub> catalyst. These results indicate that the dual-bed catalytic system produced 1-octene more efficiently and in higher conversions than the Ba/Al<sub>2</sub>O<sub>3</sub> single-bed system under a high space velocity. Owing to the strongly acidic properties of the Al<sub>2</sub>O<sub>3</sub> catalyst located at the upper site, the reduction in the 1-octanol conversion was less than that observed for the Ba/Al<sub>2</sub>O<sub>3</sub> single-bed catalyst when the LHSV was set at > 28 h<sup>–1</sup>. At the same time, the Ba/Al<sub>2</sub>O<sub>3</sub> catalyst located at the end of the catalyst bed suppressed isomer formation through the anti-Saytzeff effect. As a result, the 1-octene selectivity greatly increased to 55.8% at an LHSV of 56 h<sup>–1</sup> compared to that obtained for the Al<sub>2</sub>O<sub>3</sub> single-bed system (i.e., 38.0%). These results indicate that the dual-bed system is more advantageous in terms of increasing 1-octene production at a high LHSV.

As shown in Fig. 2, the 1-octene selectivity changed upon varying the xAl–yBa catalyst bed ratio in the dual-bed system. Upon comparison of the 50Al–50Ba and 40Al–60Ba systems, which enabled similar conversions, it was found that the 1-octene selectivity of the 40Al–60Ba system increased by 5.2% on average for the various LHSVs examined herein. However, when the Ba to Al ratio was ≥ 70%, the 1-octanol conversion decreased with the Ba to Al ratio at an LHSV of ≥ 28 h<sup>–1</sup>.

**Table 2**

Catalytic performances of the dual-bed and single-bed systems at 400 °C.

| Catalyst                          | W <sub>cat</sub><br>(g) | LHSV<br>(h <sup>-1</sup> ) | 1-octanol conversion<br>(%) | 1-octene selectivity<br>(%) | 1-octene yield<br>(%) | 1-octene purity<br>(%) | DOE selectivity<br>(%) |
|-----------------------------------|-------------------------|----------------------------|-----------------------------|-----------------------------|-----------------------|------------------------|------------------------|
| 50Al-50Ba                         | 0.6                     | 7                          | 99.7                        | 11.0                        | 11.0                  | 11.0                   | 0.0                    |
|                                   |                         | 14                         | 100.0                       | 29.6                        | 29.6                  | 29.6                   | 0.0                    |
|                                   |                         | 21                         | 99.9                        | 47.4                        | 47.4                  | 47.4                   | 0.0                    |
|                                   |                         | 28                         | 99.7                        | 53.2                        | 53.0                  | 53.2                   | 0.0                    |
|                                   |                         | 56                         | 94.5                        | 55.8                        | 52.7                  | 55.9                   | 0.3                    |
| Al <sub>2</sub> O <sub>3</sub>    | 0.3                     | 7                          | 97.3                        | 9.9                         | 9.6                   | 9.9                    | 0.0                    |
|                                   |                         | 14                         | 100.0                       | 15.1                        | 15.1                  | 15.1                   | 0.0                    |
|                                   |                         | 21                         | 100.0                       | 25.2                        | 25.2                  | 25.2                   | 0.0                    |
|                                   |                         | 28                         | 100.0                       | 34.5                        | 34.5                  | 34.5                   | 0.0                    |
|                                   |                         | 56                         | 99.2                        | 48.8                        | 48.4                  | 48.8                   | 0.0                    |
|                                   |                         | 112                        | 93.7                        | 52.8                        | 49.5                  | 52.9                   | 0.2                    |
|                                   | 0.6                     | 168                        | 83.5                        | 54.2                        | 45.3                  | 54.5                   | 0.5                    |
|                                   |                         | 7                          | 96.9                        | 6.9                         | 6.7                   | 7.0                    | 0.9                    |
|                                   |                         | 14                         | 98.9                        | 12.6                        | 12.4                  | 12.6                   | 0.3                    |
|                                   |                         | 21                         | 100.0                       | 21.7                        | 21.7                  | 21.7                   | 0.0                    |
|                                   |                         | 28                         | 99.8                        | 26.9                        | 26.8                  | 26.9                   | 0.0                    |
|                                   |                         | 56                         | 98.5                        | 38.0                        | 37.4                  | 38.1                   | 0.1                    |
|                                   | 0.3                     | 7                          | 90.8                        | 34.2                        | 31.0                  | 34.3                   | 0.4                    |
|                                   |                         | 14                         | 97.0                        | 64.7                        | 62.8                  | 64.9                   | 0.3                    |
|                                   |                         | 21                         | 95.3                        | 74.2                        | 70.7                  | 74.6                   | 0.5                    |
|                                   |                         | 28                         | 92.2                        | 77.0                        | 71.0                  | 77.6                   | 0.9                    |
|                                   |                         | 56                         | 78.8                        | 77.6                        | 61.1                  | 79.3                   | 2.1                    |
|                                   |                         | 112                        | 55.8                        | 75.1                        | 41.9                  | 77.9                   | 3.7                    |
|                                   |                         | 168                        | 44.5                        | 73.8                        | 32.8                  | 77.1                   | 4.2                    |
| Ba/Al <sub>2</sub> O <sub>3</sub> | 0.6                     | 7                          | 99.5                        | 37.4                        | 37.2                  | 37.4                   | 0.1                    |
|                                   |                         | 14                         | 98.6                        | 66.7                        | 65.8                  | 66.8                   | 0.2                    |
|                                   |                         | 21                         | 96.0                        | 73.8                        | 70.9                  | 74.2                   | 0.5                    |
|                                   |                         | 28                         | 92.3                        | 75.1                        | 69.3                  | 75.9                   | 1.0                    |
|                                   |                         | 56                         | 76.3                        | 76.8                        | 58.6                  | 79.3                   | 3.2                    |

To understand the action of the dual-bed catalyst system, the 40Al catalyst layer alone was tested at the same feed flow rates (i.e., LHSV 7–56 h<sup>-1</sup>) as those investigated for 40Al-60Ba, wherein the flow rate was identical to that of the 40Al catalyst bed tested at LHSVs of 17.5, 35, 52.5, 70, and 140 h<sup>-1</sup>. As shown in Fig. S7, the 1-octanol conversion of 40Al was similar to that of 40Al-60Ba, thereby suggesting that the majority of 1-octanol reacted in the 40Al catalyst layer of 40Al-60Ba. However, 40Al-60Ba produced a higher 1-octene fraction than 40Al (Fig. S8), and so the 1-octene selectivity appeared to be improved owing to the anti-Saytzeff effect resulting from the high basicity in the 60-Ba layer. Furthermore, the effect of the catalyst bed stacking order was also examined in different dual-bed catalytic systems, including the 60Ba-40Al, 40Al-60Ba, and 40Al + 60Ba (physical mixture) systems. However, no change in the 1-octanol conversion was observed, although the 1-octene mole fraction varied between systems. More specifically, at an LHSV of 7 h<sup>-1</sup> (Fig. S8), the isomerization proceeded more actively when the Al<sub>2</sub>O<sub>3</sub> catalyst was located at the end of the catalyst bed with a high 1-octene concentration, while the 1-octene mole fraction decreased according to reducing the Al<sub>2</sub>O<sub>3</sub> ratio at the end of the catalyst bed. Overall, it appeared that the Al-Ba system, which contained the highly acidic Al<sub>2</sub>O<sub>3</sub> at the top of the bed (high 1-octanol concentration) and Ba/Al<sub>2</sub>O<sub>3</sub> at the bottom of the bed (high 1-octene concentration), was optimal. Fig. 3 shows the product fractions obtained with a variation in the bed ratio. As indicated, catalytic systems with a high Ba to Al ratio afforded a greater fraction of 1-octene while suppressing the occurrence of side reactions. As the Ba to Al ratio was increased at all LHSVs, the proportion of the *trans*-isomer decreased, while that of the 1-octene fraction increased. In particular, at an LHSV of 21 h<sup>-1</sup>, the *trans*-isomer fraction decreased by the greatest extent, i.e., from 57.5% for the Al<sub>2</sub>O<sub>3</sub> single-bed to 31.1% for the 50Al-50Ba system. No significant changes were observed in terms of the *cis*-isomer proportion; however, the production of the *cis*-isomer decreased upon increasing the Ba to Al ratio.

As shown in Fig. 3, the 1-octene productivity was proportional to the Ba ratio in the catalyst bed at lower LHSVs (<28 h<sup>-1</sup>). Therefore, the 10Al-90Ba catalytic system, which possessed a high Ba to Al catalyst ratio, exhibited a high 1-octene productivity at LHSVs of 7–28 h<sup>-1</sup>; the product was also obtained in a high purity. More specifically, compared with the Al<sub>2</sub>O<sub>3</sub> single-bed system, the 1-octene productivity improved fivefold and the *trans*-isomer fraction decreased by half under an LHSV of 14 h<sup>-1</sup> for this dual-bed system (Fig. 3(b)).

It was also found that the 1-octene productivity increased upon increasing the 1-octene mole fraction of the product. Although the Ba/Al<sub>2</sub>O<sub>3</sub> catalyst showed the highest 1-octene productivity at LHSVs of 7–28 h<sup>-1</sup>, at high LHSVs of >21 h<sup>-1</sup>, the 1-octanol conversion decreased due to the high Ba to Al catalyst bed ratio of 90%. In this respect, the 40Al-60Ba system was found to be advantageous because it affords a higher 1-octanol conversion owing to the presence of numerous LASs. This catalytic system exhibited a higher 1-octene productivity (3495.2 g<sub>1-octene</sub>/g<sub>cat</sub> h) than the Ba/Al<sub>2</sub>O<sub>3</sub> catalyst (3439.4 g<sub>1-octene</sub>/g<sub>cat</sub> h) under an LHSV of 56 h<sup>-1</sup>. These results therefore indicate that the optimal catalyst ratio differed according to the LHSV conditions.

#### Assessment of the 1-octene selectivity

An assessment of the catalytic performance in TOS for 100 h was then performed on the single-bed (Al<sub>2</sub>O<sub>3</sub>, Ba/Al<sub>2</sub>O<sub>3</sub>) and dual-bed (40Al-60Ba, 10Al-90Ba) catalytic systems that yielded high 1-octene productivities (Table 3 and Fig. 4). As indicated, no significant changes in the 1-octanol conversion were observed over a TOS of 100 h for either the Al<sub>2</sub>O<sub>3</sub> or the Ba/Al<sub>2</sub>O<sub>3</sub> single-bed systems; however, a different trend was observed for the 1-octene selectivity. More specifically, the 1-octene selectivity of the Al<sub>2</sub>O<sub>3</sub> catalyst was very low, and it changed only slightly with a TOS of 100 h. In contrast, the initially high 1-octene selectivity exhibited by the Ba/Al<sub>2</sub>O<sub>3</sub> catalyst decreased with a longer TOS. Both possible

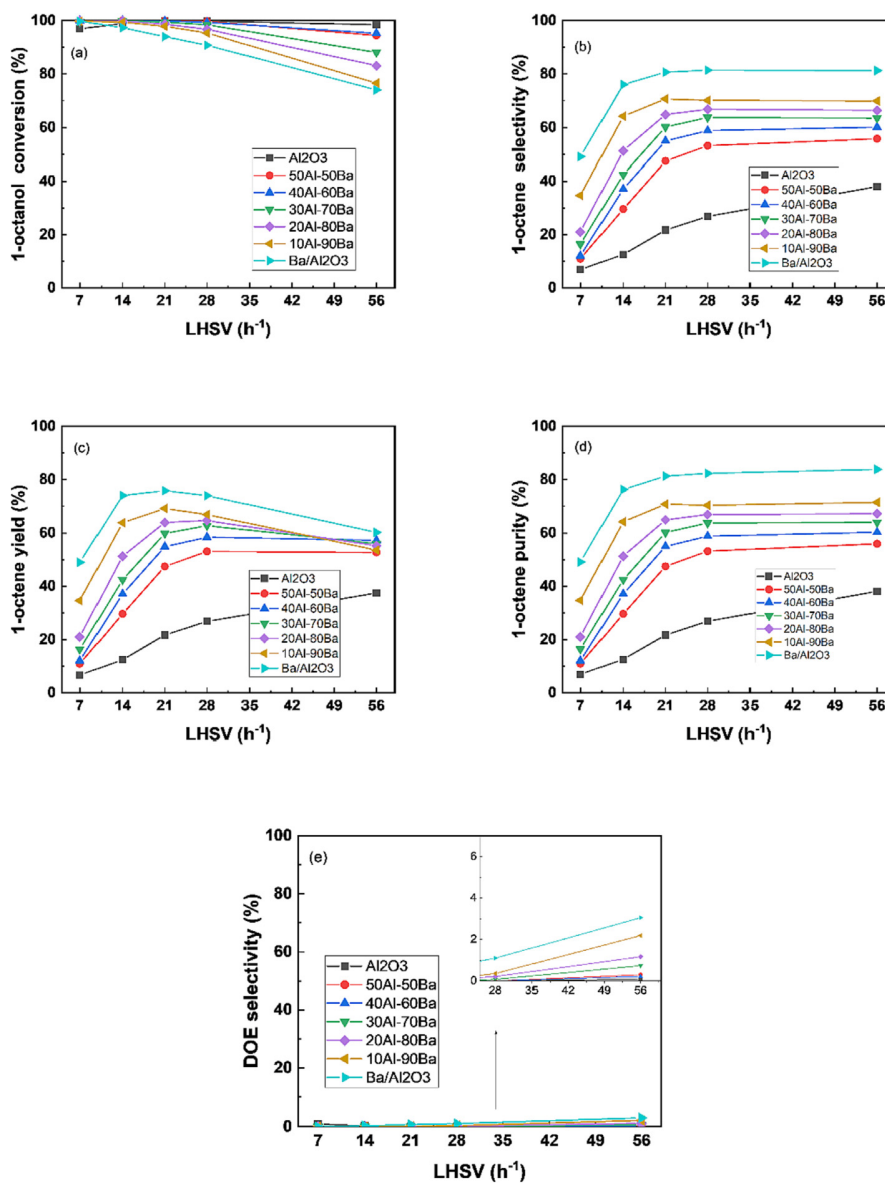


**Fig. 2.** Effect of the LHSV on (a) the 1-octanol conversion, (b) the 1-octene selectivity, (c) the 1-octene yield, (d) the 1-octene purity, and (e) the DOE selectivity upon variation in the dual-bed ratio ( $T_{\text{cat}} = 400^\circ\text{C}$ ,  $W_{\text{cat}} = 0.6\text{ g}$ ,  $\text{TOS} = 2\text{ h}$ ).

mechanisms of deactivation (i.e., coking and learning) were therefore considered for the Ba/Al<sub>2</sub>O<sub>3</sub> catalyst. More specifically, to examine the effect on coking, the spent catalyst was analyzed by Raman spectroscopy and TGA (Fig. S9). The Raman results indicated that two peaks corresponding to the produced coke were observed, i.e., at 1338 and 1604 cm<sup>-1</sup> [37,38]. These peaks gave  $I_{\text{D}}/I_{\text{G}}$  ratios < 1 due to the graphite-like structure of the coke [39,40], which in turn was attributed to alkene polymerization and subsequent coke deposition [41]. However, the degree of coke formation was comparable on the surface of the spent Al<sub>2</sub>O<sub>3</sub> catalyst, with coke amounts of 0.081 and 0.085 gC/g<sub>cat</sub> being determined for the Ba/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> catalysts, respectively. As illustrated in Fig. 4, the Al<sub>2</sub>O<sub>3</sub> catalyst exhibited a relatively stable activity over the initial 100 h on-stream, and so it appeared that the effect of coke formation on the deactivation of the Ba/Al<sub>2</sub>O<sub>3</sub> catalyst was insignificant. Additionally, based on the ICP analysis results (Table S1) for the spent Ba/Al<sub>2</sub>O<sub>3</sub> catalyst, it was confirmed that the Ba content was reduced from 1.5 to 1.2 wt%, indicating

that the 1-octene selectivity decreased owing to the loss of Ba and subsequent catalyst deactivation. As expected, the dual-bed system yielded a higher and more stable 1-octene selectivity than the single-bed systems evaluated in these TOS tests. Although the 1-octene selectivity, yield, and purity of the dual-bed system became lower than those of the Ba/Al<sub>2</sub>O<sub>3</sub> single-bed system after 3 h (Table 3), throughout all these catalytic tests, the dual-bed system exhibited a reduced decrease in its 1-octene selectivity compared to that shown by the single-bed Ba/Al<sub>2</sub>O<sub>3</sub> systems. As mentioned above, in the case of the dual-bed system, almost full 1-octanol conversion was achieved at the Al<sub>2</sub>O<sub>3</sub> catalyst located at the upper site, while 1-octene selectivity and stability improved because for the Ba/Al<sub>2</sub>O<sub>3</sub> catalyst due to its higher basicity. In particular, the 10Al-90Ba dual-bed system exhibited a lower reduction in the 1-octene yield (i.e., 16.9% reduction) yield than the Ba/Al<sub>2</sub>O<sub>3</sub> single-bed system (i.e., 25.9% reduction) after a TOS of 100 h. However, as the results for the Ba/Al<sub>2</sub>O<sub>3</sub> and 10Al-90Ba systems were generally indistinguishable between 60 and 100 h TOS,

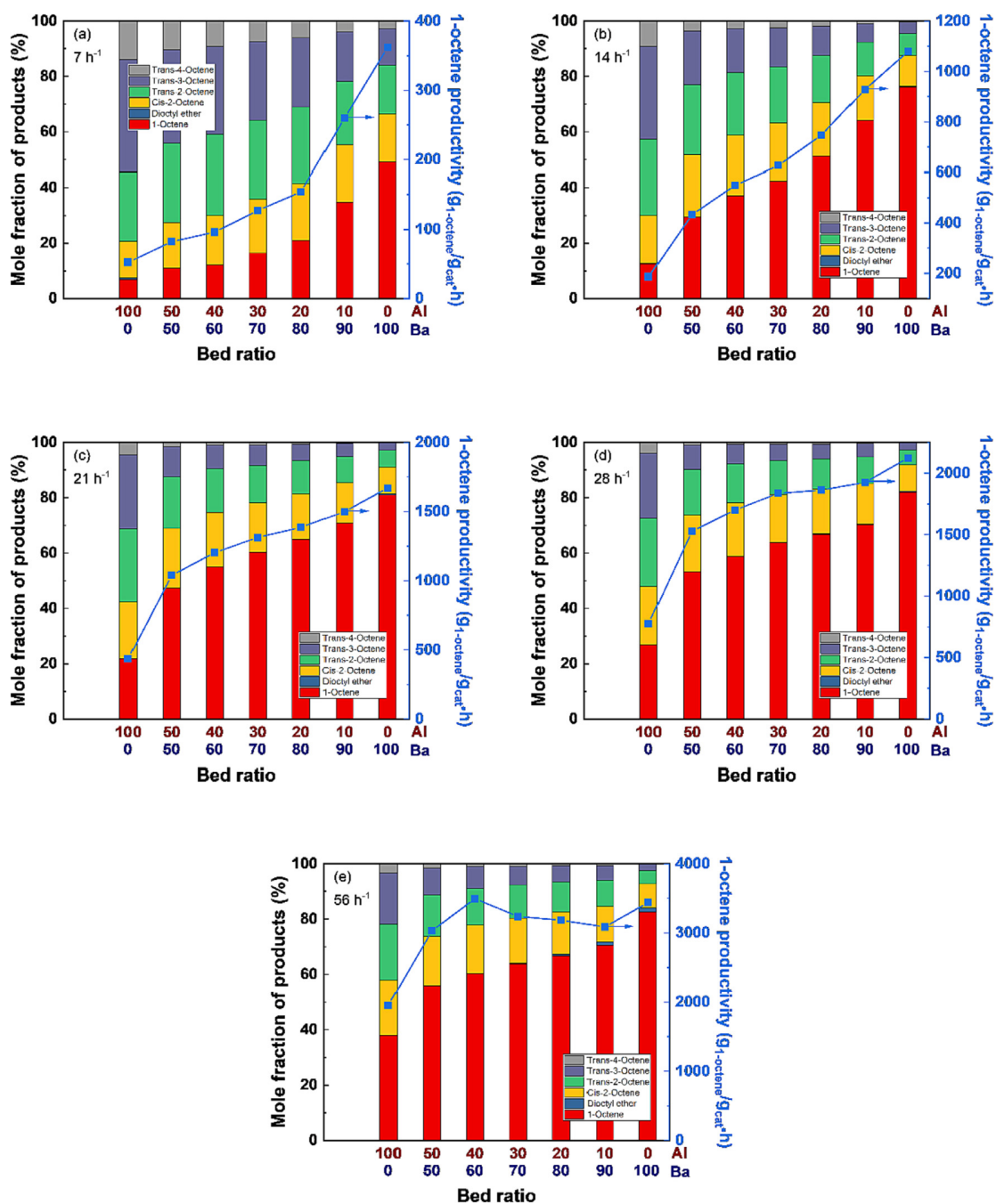


Fig. 3. Effect of the dual-bed ratio on product mole fractions and the 1-octene productivity at 400 °C with LHSV of 7–56 h<sup>-1</sup> ( $T_{\text{cat}} = 400$  °C,  $W_{\text{cat}} = 0.6$  g, TOS = 2 h).

Table 3

Effect of the TOS on the catalytic activities of the dual-bed and single-bed catalytic systems ( $T_{\text{cat}} = 400$  °C, LHSV = 21 h<sup>-1</sup>,  $W_{\text{cat}} = 0.6$  g, TOS = 100 h).

| Catalytic system                  | 1-Octanol conversion (%) |       | 1-Octene selectivity (%) |       | 1-Octene yield (%) |       | 1-Octene purity (%) |       |
|-----------------------------------|--------------------------|-------|--------------------------|-------|--------------------|-------|---------------------|-------|
|                                   | 3 h                      | 100 h | 3 h                      | 100 h | 3 h                | 100 h | 3 h                 | 100 h |
| Al <sub>2</sub> O <sub>3</sub>    | 100.0                    | 97.8  | 20.8                     | 29.4  | 20.8               | 28.7  | 20.8                | 29.4  |
| 40Al-60Ba                         | 99.4                     | 90.5  | 57.1                     | 45.4  | 56.8               | 40.8  | 57.1                | 45.6  |
| 10Al-90Ba                         | 94.5                     | 90.1  | 75.1                     | 58.8  | 71.0               | 53.0  | 75.4                | 59.1  |
| Ba/Al <sub>2</sub> O <sub>3</sub> | 89.5                     | 91.7  | 89.8                     | 59.4  | 80.4               | 54.4  | 91.2                | 59.7  |

their final 1-octene selectivities and yields were similar. Therefore, in terms of the catalytic deactivation mechanism, further investigation into the initial rapid deactivation is required in the future.

As shown in Fig. 5, for the Al<sub>2</sub>O<sub>3</sub> catalyst single-bed systems employed over longer TOSs, the change in the product fraction tended to involve an increase in the overall fraction of the *trans*-

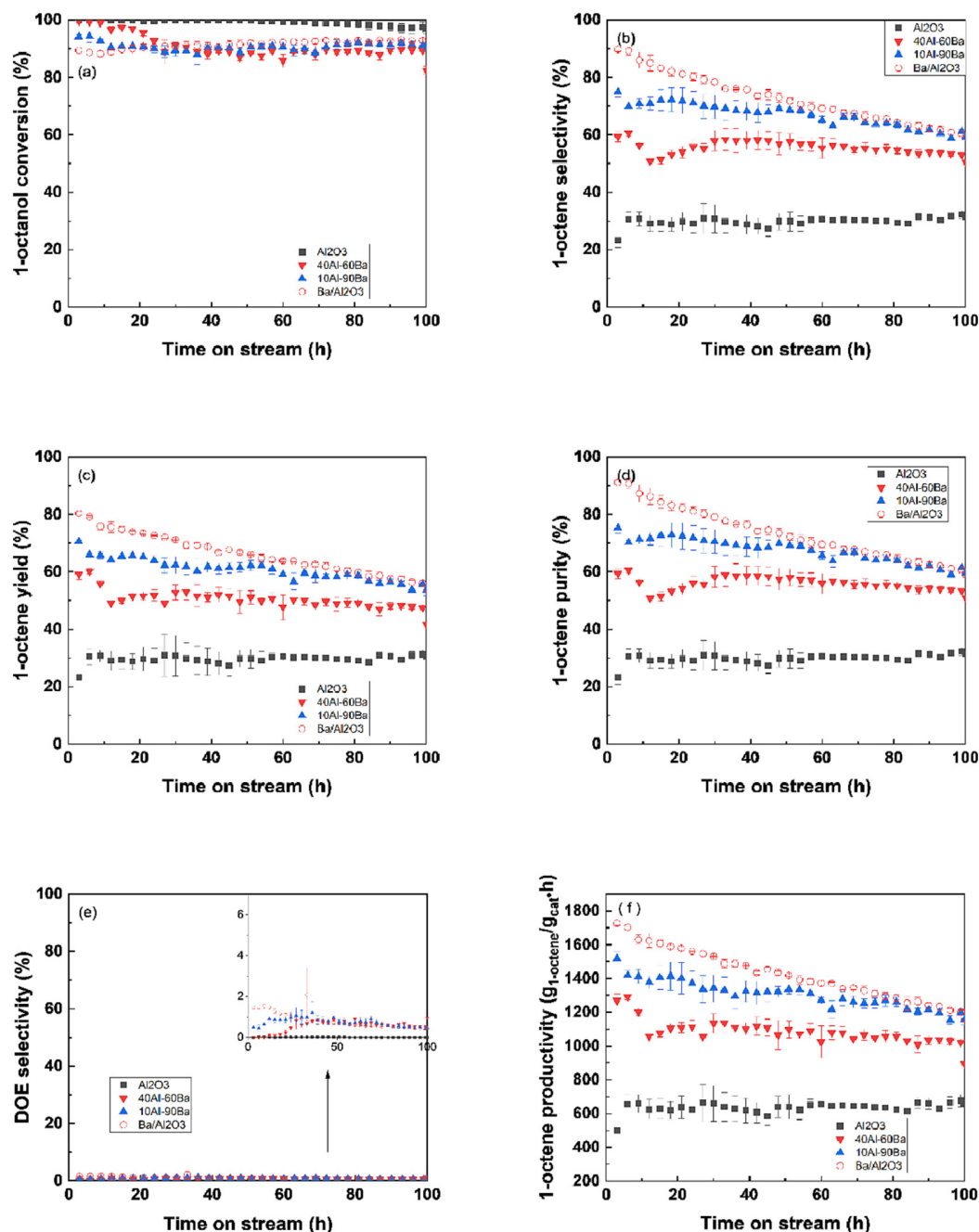


**Fig. 4.** (a) the 1-octanol conversion, (b) the 1-octene selectivity, (c) the 1-octene yield, (d) the 1-octene purity, (e) the DOE selectivity, and (f) the 1-octene productivity) of the dual-bed and single-bed catalytic systems in TOS test ( $T_{\text{cat}} = 400^\circ\text{C}$ ,  $\text{LHSV} = 21\text{ h}^{-1}$ ,  $\text{TOS} = 100\text{ h}$ ,  $W_{\text{cat}} = 0.6\text{ g}$ ).

isomer and a reduction in the 1-octene fraction. This change was attributed to the thermodynamic instability of 1-octene. In addition, a small fraction of DOE was formed even in the 10Al-90Ba catalytic system, which yielded the highest fraction of 1-octene. This may be attributed to the fact that when 1-octanol passes through the upper  $\text{Al}_2\text{O}_3$  catalyst layer in the dual-bed system, the majority of reactants are converted into olefins. Subsequently, in the lower Ba/ $\text{Al}_2\text{O}_3$  layer, isomer formation was suppressed through the anti-Saytzeff effect, thereby ensuring that a high 1-olefin fraction was maintained.

## Conclusion

A dual-bed catalytic system based on  $\text{Al}_2\text{O}_3$  and Ba/ $\text{Al}_2\text{O}_3$  catalysts was developed for the production of high-purity 1-octene through the dehydration of 1-octanol, and this dual-bed system was found to afford a higher yield of 1-octene than the corresponding single-bed catalytic systems. Upon increasing the 1-olefin residence time by the use of a more catalyst bed, the side reaction caused by olefin re-adsorption occurred to a greater extent. As a result, the 1-octene selectivity of the  $\text{Al}_2\text{O}_3$  catalyst decreased with

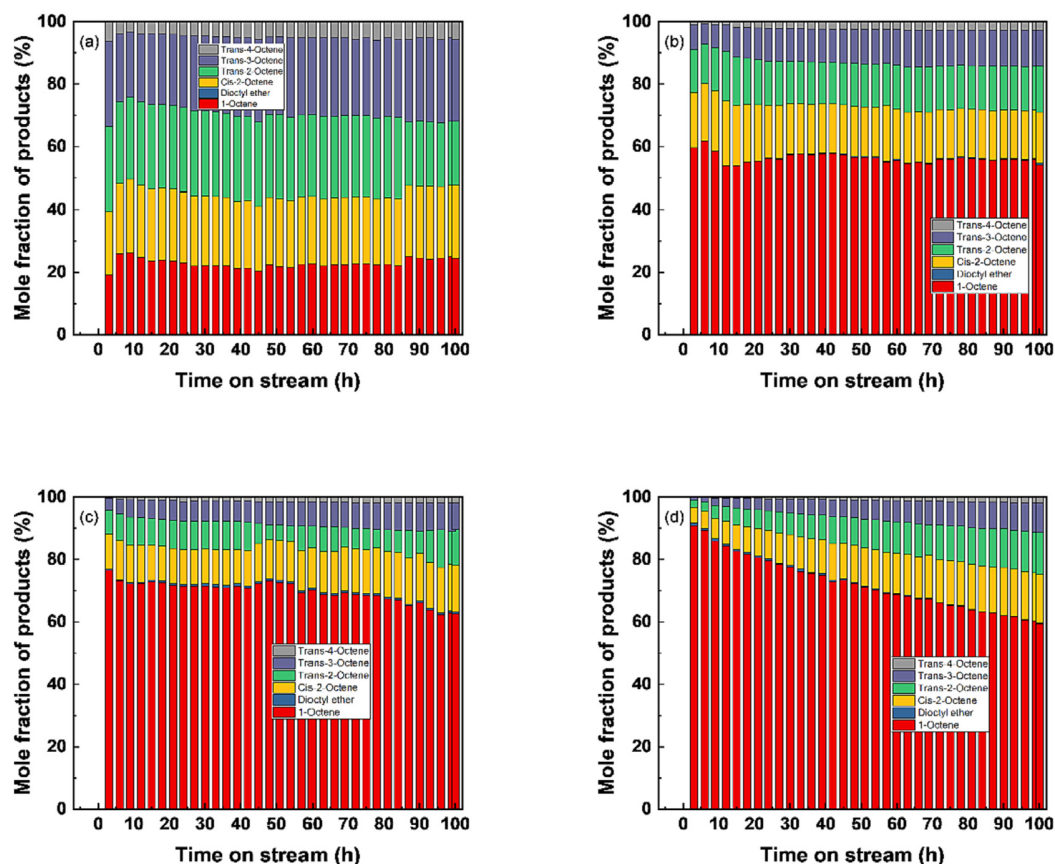


**Fig. 5.** Effect of the time-on-stream on the product distributions of the (a)  $\text{Al}_2\text{O}_3$ , (b) 40Al-60Ba, (c) 10Al-90Ba, and (d) Ba/ $\text{Al}_2\text{O}_3$  systems ( $T_{\text{cat}} = 400^\circ\text{C}$ , LHSV =  $21\text{ h}^{-1}$ , TOS = 100 h,  $W_{\text{cat}} = 0.6\text{ g}$ ).

an increasing weight of the catalyst bed, whereas the Ba/ $\text{Al}_2\text{O}_3$  catalyst exhibited an enhanced 1-octene selectivity through the anti-Saytzeff effect. Thus, in the dual-bed system, an increase in the ratio of Ba to Al reduced the degree of isomerization compared to the single-bed  $\text{Al}_2\text{O}_3$  catalyst. Because the 1-octene purity and productivity increased at higher Ba ratios, the catalytic activity of the 10Al-90Ba catalyst was optimal over the LHSV range of 7–28  $\text{h}^{-1}$ . However, the 40Al-60Ba catalytic system with a high  $\text{Al}_2\text{O}_3$  content yielded the highest 1-octene productivity ( $3495.2\text{ g}_{1\text{-octene}}/\text{g}_{\text{cat}}\cdot\text{h}$ ) at a high LHSV of  $56\text{ h}^{-1}$ . Furthermore, the 1-octene selectivities of the single-bed Ba/ $\text{Al}_2\text{O}_3$  catalysts were reduced upon increasing the TOS. Although the use of the optimal dual-bed system resulted in a lower 1-octanol conversion than the use of single-bed systems, the dual-bed system maintained a higher 1-octene selectivity. Overall, the 10Al-90Ba dual-bed system exhibited a stable catalytic performance despite a small decrease in the 1-octene selectivity over 100 h, thereby yielding the desired 1-octene product in a high purity, and simplifying the product separation process. It is therefore expected that this dual-bed system could produce high-purity LAO products without operating under the low conversion conditions required to reduce the re-adsorption of 1-octene.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgment

This work was supported in part by the Technology Innovation Program (20012971, Development of Technology for Production of High Purity Linear) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) and the National Research Foundation of Korea (NRF) through Grants funded by the Korean Government (No.NRF-2019R1A2C2086827).

#### Appendix A. Supplementary material

Supplementary material to this article can be found online at <https://doi.org/10.1016/j.jiec.2022.11.060>.

#### Reference

- [1] L.M. Farrell, Developments in linear alpha olefin (LAO) comonomer technologies for polyethylene, NEXANT, 2012.
- [2] D.J. McClelland, B.-X. Wang, W.T. Cordell, Y.R. Cortes-Peña, E.B. Gilcher, L. Zhang, J.S. Guest, B.F. Pfeiffer, G.W. Huber, J.A. Dumesic, Green Chem. 23 (2021) 4338–4354, <https://doi.org/10.1039/d1gc00243k>.
- [3] F.S. Golub, V.A. Bolotov, V.N. Parmon, Catal. Ind. 13 (2021) 203–215, <https://doi.org/10.1134/s2070050421030053>.
- [4] P.W.N.M. van Leeuwen, N.D. Clément, M.J.L. Tschan, Coord. Chem. Rev. 255 (2011) 1499–1517, <https://doi.org/10.1016/j.ccr.2010.10.009>.
- [5] L.M. Farrell, Linear alpha olefins, Nexant, 2019.
- [6] P. Gupta, G.L. Wilkes, A.M. Sukhadia, R.K. Krishnaswamy, M.J. Lamborn, S.M. Wharry, C.C. Tso, P.J. DesLauriers, T. Mansfield, F.L. Beyer, Polymer 46 (2005) 8819–8837, <https://doi.org/10.1016/j.polymer.2005.05.137>.
- [7] A. Tesarikova, D. Merinska, J. Kalous, P. Svoboda, J. Nanomater. 2016 (2016), <https://doi.org/10.1155/2016/6014064>.

- [8] R. Long, S. Long, L. Zou, Z. Huang, Y. Huang, C. Hu, D. Li, X. Li, *Polymer* 243 (2022).
- [9] P. Svoboda, R. Theravalappil, D. Svobodova, P. Mokrejs, K. Kolomaznik, K. Mori, T. Ougizawa, T. Inoue, *Polym. Test.* 29 (2010) 742–748, <https://doi.org/10.1016/j.polymertesting.2010.05.014>.
- [10] G. Belov, P. Matkovsky, *Pet. Chem.* 50 (2010), <https://doi.org/10.1134/S0965544110040055>.
- [11] A. Jonathan, N.M. Eagan, D.L. Bruns, S.S. Stahl, M.P. Lanci, J.A. Dumesic, G.W. Huber, *Cat. Sci. Technol.* 11 (2021) 3599–3608, <https://doi.org/10.1039/d1cy00207d>.
- [12] T. Dietel, F. Lukas, W.P. Kretschmer, R. Kempe, *Science* 375 (2022) 1021–1024, <https://doi.org/10.1126/science.abm5281>.
- [13] C. Zhang, M. Xu, Z. Yang, M. Zhu, J. Gao, Y.-F. Han, *Appl. Catal. B* 295 (2021), <https://doi.org/10.1016/j.apcatb.2021.120287>.
- [14] V. Komarewsky, S. Uhlick, M. Murray, *J. Am. Chem. Soc.* 67 (1945) 557–558, <https://doi.org/10.1021/ja01220a018>.
- [15] J.T. Vossen, A.J. Vorholt, W. Leitner, *ACS Sustain. Chem. Eng.* 10 (2022) 5922–5931.
- [16] A. de Klerk, *Top. Catal.* 57 (2013) 715–722, <https://doi.org/10.1007/s11244-013-0228-6>.
- [17] R.J. Nel, A. de Klerk, *Ind. Eng. Chem. Res.* 48 (2009) 5230–5238, <https://doi.org/10.1021/ie801930r>.
- [18] H.-J. Lee, I.-H. Choi, S.-W. Kim, K.-R. Hwang, *Polymers* 13 (2021) 2850.
- [19] H.A. Dabbagh, B.H. Davis, *J. Catal.* 110 (1988), [https://doi.org/10.1016/0021-9517\(88\)90334-X](https://doi.org/10.1016/0021-9517(88)90334-X).
- [20] P. Berteau, S. Ceckiewicz, B. Delmon, *Appl. Catal.* 31 (1987) 361–383, [https://doi.org/10.1016/S0166-9834\(00\)80702-2](https://doi.org/10.1016/S0166-9834(00)80702-2).
- [21] Y.-E. Kim, U. Jung, D. Song, H.B. Im, J.C. Park, M. Hye Youn, H.-D. Jeong, G.B. Rhim, D.H. Chun, D.-W. Lee, K.B. Lee, K.Y. Koo, *Fuel* 281 (2020), <https://doi.org/10.1016/j.fuel.2020.118791>.
- [22] Y.-E. Kim, H.B. Im, U.H. Jung, J.C. Park, M.H. Youn, H.-D. Jeong, D.-W. Lee, G.B. Rhim, D.H. Chun, K.B. Lee, *Fuel* 256 (2019), <https://doi.org/10.1016/j.fuel.2019.115957>.
- [23] J. Ancheyta, J.G. Speight, *Hydroprocessing of Heavy Oils and Residua*, CRC Press, 2007.
- [24] A. Mukherjee, K. Roy, J. Bagchi, K. Mondal, *J. Res.* 2 (2016).
- [25] M.J. Kaiser, A. de Klerk, J.H. Gary, G.E. Handwerk, *Petroleum Refining: Technology, Economics, and Markets*, Sixth Edition., CRC Press, 2019.
- [26] N.A. Haji Morni, C.M. Yeung, H. Tian, Y. Yang, N. Phusunti, M.S. Abu Bakar, A.K. Azad, *J. Energy Inst.* 94 (2021) 387–397, <https://doi.org/10.1016/j.joei.2020.10.005>.
- [27] S.-T. Tsai, P.-H. Chao, I. Wang, T.-C. Tsai, *Appl. Catal. A* 385 (2010) 73–79, <https://doi.org/10.1016/j.apcata.2010.06.047>.
- [28] F. Zeng, S.H. Bossmann, M.G. Heidlage, K.L. Hohn, *Chem. Eng. Sci.* 175 (2018) 387–395, <https://doi.org/10.1016/j.ces.2017.10.009>.
- [29] G.M. Cabello González, A.L. Villanueva Perales, A. Martínez, M. Campoy, F. Vidal-Barrero, *Fuel Process. Technol.* 226 (2022), <https://doi.org/10.1016/j.fuproc.2021.107092>.
- [30] A. de Reviere, D. Gunst, M. Sabbe, A. Verberckmoes, *J. Ind. Eng. Chem.* 89 (2020) 257–272.
- [31] S.C. Shen, X. Chen, S. Kawi, *Langmuir* 20 (2004) 9130–9137, <https://doi.org/10.1021/la049947v>.
- [32] Y. Ni, Y. Liu, Z. Chen, M. Yang, H. Liu, Y. He, Y. Fu, W. Zhu, Z. Liu, *ACS Catal.* 9 (2019) 1026–1032, <https://doi.org/10.1021/acscatal.8b04794>.
- [33] F. Prinetto, G. Ghiotti, R. Durand, D. Tichit, *J. Phys. Chem. B* 104 (2000) 11117–11126, <https://doi.org/10.1021/jp002715u>.
- [35] B.H. Davis, *J. Org. Chem.* 47 (1982) 900–902.
- [36] B.C. Shi, B.H. Davis, *J. Catal.* 157 (1995) 359–367, <https://doi.org/10.1006/jcat.1995.1301>.
- [37] Y.T. Chua, P.C. Stair, *J. Catal.* 213 (2003) 39–46.
- [38] C.C. Zhang, S. Hartlaub, I. Petrovic, B. Yilmaz, *ACS Omega* 7 (2022) 2565–2570, <https://doi.org/10.1021/acsomega.1c03456>.
- [39] P.P. Paalanen, S.H. Van Vreeswijk, B.M. Weckhuysen, *ACS Catal.* 10 (2020) 9837–9855, <https://doi.org/10.1021/acscatal.0c01851>.
- [40] R. Escobano, J. Sloan, N. Siddique, N. Sze, T. Dudev, *Vib. Spectrosc* 26 (2001) 179–186.
- [41] C.E. Li, T.C. Brown, *Energy Fuels* 13 (1999) 888–894.