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Dual bed catalyst system for oxidative dehydrogenation of mixed-butenes: a synergistic mechanism*

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Abstract: Oxidative dehydrogenation (ODH) of mono and mixed-butenes to 1,3-butadiene (BD) was conducted using individual and dual bed catalyst systems, consisting of $ZnFe_2O_4$, $Co_9Fe_3Bi_1Mo_{12}O_{51}$ or both. The dual bed catalyst system gave improved catalytic performance. A mechanism based on synergy between the catalysts is proposed to explain the improved overall butene conversion. The proportion of the reactants differed between the catalyst beds in the dual bed system, making better use of the catalytic activity of the second bed. The existence of all butene isomers inhibited isomerization, leading to a higher proportion of ODH reactions and thus improved the conversion of butene and the yield of BD. The packing sequences and the volume ratio of the catalysts in the bed were optimized. The results indicated that the sequence with $ZnFe_2O_4$ on top and a catalyst packing ratio of between 4:6 and 6:4 led to better activity.

Key words: Mixed-butenes; Dual bed catalyst; Oxidative dehydrogenation (ODH); Synergistic effect
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1 Introduction

The conversion of methanol to olefin (MTO), a crucial process in the modern coal chemical industry, has been successfully industrialized on a large scale. Among the byproducts of MTO, there is a considerable amount of C4 hydrocarbons containing a high proportion of 1-butene, trans-2-butene, and cis-2-butene (Tu and Li, 2012). The similar physical properties of butene isomers make them quite difficult to separate or purify. Thus, the development of an efficient technology to convert or use butene isomers simultaneously is a challenging research topic.

According to the existing data, catalytic oxidation (Yu *et al.*, 2011), especially oxidative dehydrogenation (ODH) of specific butene to 1,3-butadiene has been demonstrated to be an effective way to use C4 hydrocarbons (Toledo *et al.*, 1995; 1997; 2000), since 1,3-butadiene is an essential feedstock to produce some high-valued materials like styrene butadiene rubber. Some catalysts with high performance have been developed based on this reaction (Wan *et al.*, 2015a; 2015b; 2016a; 2016b). Bismuth molybdates (Batist *et al.*, 1966; 1967; 1968; 1969) and ferrites (Hong *et al.*, 1984; Yang *et al.*, 1984) are the most extensively investigated catalysts among those reported. Their catalytic activity differs from each other towards different butene isomers. For example, $Co_9Fe_3Bi_1Mo_{12}O_{51}$ exhibited a better activity in ODH of 1-butene than of 2-butene (Jung *et al.*, 2008b). $ZnFe_2O_4$ showed high activity in the ODH of both cis-2-butene (Kung *et al.*, 1980; 1981) and trans-2-butene (Cares and Hightower, 1971). Thus, it

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ORCID: Xiao-yi LI, http://orcid.org/0000-0002-9133-6321 can be expected that the combination of these two series catalysts might improve the conversion of mixed-butenes.

Recently, a dual bed catalyst system was developed for some significant reactions like methane conversion (Tong *et al.*, 2005; Arpornwichanop *et al.*, 2011; Ji and Wang, 2012; Zohour *et al.*, 2014), lean burn natural gas exhaust removal (Gawade *et al.*, 2012; Zohour *et al.*, 2014), and aromatic hydrocarbon trans-alkylation (Ali *et al.*, 2015). This system is characterized by packing two catalysts into one bed in certain sequences, which makes it efficient for converting reactants with differing composition. A dual bed containing $Co_9Fe_3Bi_1Mo_{12}O_{51}$ and $ZnFe_2O_4$ may lead to good performance in ODH of butene isomers.

A synergistic effect of using this catalyst system for ODH of C4 raffinate-3 was demonstrated and a preliminary explanation was proposed (Jung *et al.*, 2008b). To the best of our knowledge, aside from the ODH and combustion process, isomerization was also included in the reaction system (Kung *et al.*, 1980; Zhang *et al.*, 1985). Thus, this study aimed to investigate the effects of isomers and isomerization on the ODH performance of a dual bed catalyst system for converting mixed-butenes. The concentration of butenes varied between the catalyst beds. This variation may enhance the performance of the second catalyst bed and thus improve the overall yield of 1,3-butadiene (BD). The existence of all butene isomers may also inhibit isomerization, improving the selectivity of ODH reaction. A series of experiments were conducted to prove such a mechanism. To obtain a higher yield of BD, the packing sequence of volume catalysts was also optimized.

2 Materials and methods

2.1 Materials

Zinc nitrate ($Zn(NO_3)_2\cdot 6H_2O$), ferric nitrate ($Fe(NO_3)_3\cdot 9H_2O$), cobalt nitrate ($Co(NO_3)_2\cdot 6H_2O$), bismuth nitrate ($Bi(NO_3)_3\cdot 5H_2O$), ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), ethylene glycol monomethyl ether ($C_3H_8O_2$), and mono-ethanolamine (C_2H_7NO) were all obtained from Sinopharm Chemical Reagent Co. Ltd., China and used without further purification.

2.2 Catalyst preparation

$ZnFe_2O_4$ was prepared by a water-free method (Li *et al.*, 2011). First, 2.16 g $Zn(CH_3COO)_2\cdot 2H_2O$ and 8.08 g $Fe(NO_3)_3\cdot 9H_2O$ were dissolved in 200 mL of ethylene glycol monomethylether, and 0.62 g of mono-ethanolamine was introduced as a complexing agent. After vigorously stirring for 4 h, the solution was transferred into several crucibles. The solvent was evaporated after heating in a muffle furnace at 300 °C for 2 h. The remaining substance was further calcined at 650 °C for 6 h to obtain $ZnFe_2O_4$ catalyst.

$Co_9Fe_3Bi_1Mo_{12}O_{51}$ was prepared by a co-precipitation method (Jung *et al.*, 2008a). Typically, 1.5 g $Bi(NO_3)_3\cdot 5H_2O$ was dissolved in 10 mL of distilled water acidified with 3 mL of concentrated nitric acid. The solution was then added to 100 mL of an aqueous solution containing 7.9 g $Co(NO_3)_2\cdot 6H_2O$ and 3.7 g $Fe(NO_3)_3\cdot 9H_2O$ to obtain a mixed nitrate solution. The mixed nitrate solution was added dropwise to 50 mL of an aqueous solution containing 6.4 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ under vigorous stirring. After stirring the mixed solution vigorously at room temperature for 1 h, a solid product was obtained by evaporation. The solid product was dried overnight at 175 °C, and was then calcined at 475 °C for 5 h in an air stream to yield a $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst. All prepared catalysts were pressed into 40–60 meshes for testing.

2.3 Characterization

The formation of $ZnFe_2O_4$ and $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts was determined by X-ray diffraction (XRD) (PANalytical B.V. Empyrean, the Netherlands) measurements. The atomic ratios of metal components in the prepared catalysts were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Thermo iCAP 6300, USA).

The oxidative dehydrogenation reaction was conducted in a continuous fixed-bed downstream reactor, in which the reaction gas flowed straight down through the catalyst bed. Water was sufficiently vaporized by passing through a pre-heating zone and was continuously fed into the reactor. The choice of butene source depended on the reaction conditions, and included 1-butene, trans-2-butene, or cis-2-butene. Also, the mixed-butenes consisted of all the above at a ratio of 6.5/11.2/8.3 (1-butene/trans-2-butene/cis-2-butene). This simulated the exact product composition of MTO C4 byproduct (Tu and Li, 2012). Air was used as an oxygen source (nitrogen in the air served as a carrier gas). The feed composition was fixed at 1/0.82/10.4 (butene/oxygen/steam) (Wan *et al.*, 2015a; 2016a) with a total gas flow rate of 112.5 mL/min.

Prior to the catalytic reaction, the catalyst bed was pretreated at 470 °C for 1 h with air and steam of reaction conditions. The catalytic reaction was conducted at 375 °C. The gas hourly space velocity (GHSV) was fixed at 438 h^{-1} on the basis of butene (Wan *et al.*, 2015a; 2016a) with a catalyst loading of 1.5 g. In the dual bed catalyst system, the volume of each catalyst was half of that in the single-bed catalyst system, while the total volume was unchanged. Reaction products were periodically sampled and analyzed using gas chromatography. Conversion of butene and its isomers, and yield and selectivity of 1,3-butadiene and carbon dioxide were calculated on the basis of the carbon balance.

3 Results and discussion

3.1 Characterization of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ and $ZnFe_2O_4$ catalysts

The formation of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ and $ZnFe_2O_4$ catalysts was determined by XRD and ICP-AES.

Fig. 1 presents the XRD patterns of $ZnFe_2O_4$ and $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts. Each phase was identified by its characteristic diffraction peaks using Joint Committee on Powder Diffraction Standards (JCPDS). The $ZnFe_2O_4$ catalyst retained a pure zinc ferrite ($ZnFe_2O_4$) phase, and the $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst was composed of four major mixed phases of β-$CoMoO_4$, α-$CoMoO_4$, $Fe_2(MoO_4)_3$, and γ-Bi_2MoO_6. These results are consistent with those of previous reports (Jung *et al.*, 2008a). The atomic ratio of Fe/Zn in the $ZnFe_2O_4$ catalyst by ICP was 2.09/1.0, which was in good agreement with the theoretical value of 2.0/1.0. The atomic ratio of Co/Fe/Bi/Mo in the $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst was measured to be 9.0/3.1/1.1/11.8. The above results indicated that $ZnFe_2O_4$ and $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalysts had been successfully prepared.

3.2 Performance of individual and dual bed catalyst systems in ODH of individual butene isomers

Fig. 2 presents the activity of single and dual bed catalyst systems in 1-butene ODH.

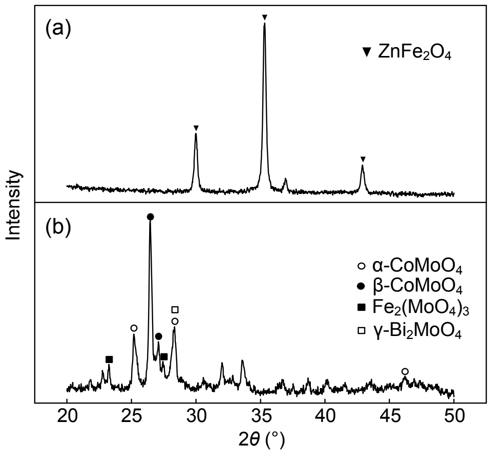

Fig. 1 XRD patterns of $ZnFe_2O_4$ (a) and $Co_9Fe_3Bi_1Mo_{12}O_{51}$ (b) catalysts

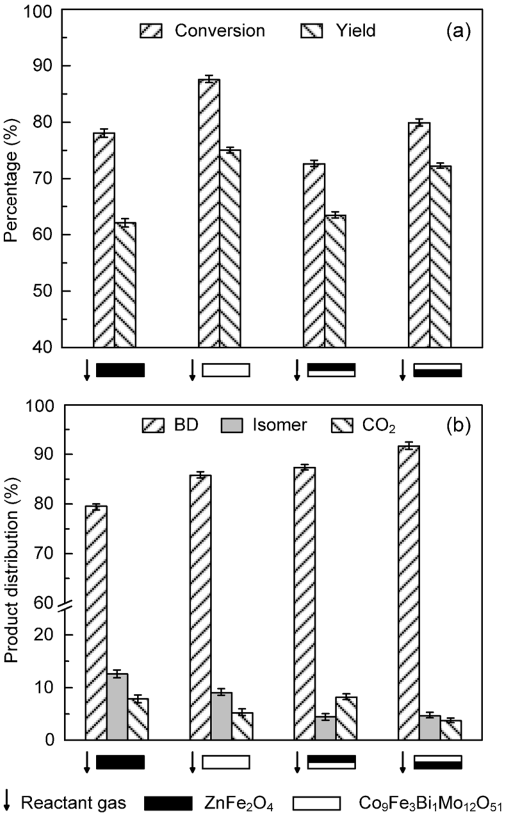

Fig. 2 ODH of 1-butene over different catalyst systems
(a) Conversion of 1-butene and yield of BD; (b) Product distribution of BD, butene isomers, and CO_2. Reaction conditions: butene/oxygen/steam=1/0.82/10.4; reaction temperature is 375 °C; GHSV is 438 h^{-1} on the basis of butene

Of the two single bed systems, the one using $Co_9Fe_3Bi_1Mo_{12}O_{51}$, showed a higher catalytic activity. In the temperature programmed desorption (TPD) analysis of Jung *et al.* (2008b), $Co_9Fe_3Bi_1Mo_{12}O_{51}$ was proved to contain more selective oxygen species for 1-butene, yet the amount of active sites for combustion stayed relatively the same as $ZnFe_2O_4$. This enhanced performance in 1-butene adsorption and BD selectivity contributed to the high yield of BD. The products also contained a certain amount of isomers from the isomerization of 1-butene. The dual bed system shared a similar activity but an increased selectivity of BD. This could be explained by the ODH of 2-butenes in the second bed. Take the packing sequence where $ZnFe_2O_4$ was packed as the second bed as an example. The adsorption of 2-butenes, especially cis-2-butene, is stronger than that of 1-butene on the surface of $ZnFe_2O_4$ (Zhou *et al.*, 1983). This means the isomers created by the first bed could have had a better ODH conversion on the second bed. Meanwhile, the existing 1-butene could also be converted efficiently. The combined effects would lead to a higher selectivity of BD and a higher conversion of 1-butene. Thus, for the ODH of 1-butene, packing $Co_9Fe_3Bi_1Mo_{12}O_{51}$ on top would result in a better yield of BD.

Figs. 3 and 4 show ODH results of trans-2-butene and cis-2-butene over the single and dual bed catalyst systems, respectively. Clearly, $ZnFe_2O_4$ had a higher activity in ODH of both 2-butenes. The ODH process of butenes on $ZnFe_2O_4$ requires the formation of π-allyl groups on the Fe-O bond. According to the Rennard-Massoth mechanism (Massoth and Scarpiello, 1971; Rennard and Kehl, 1971), the controlling step in the formation of such groups is the homolysis of the first hydrogen atom. Also, trans-2-butene has a lower energy requirement for this process than cis-2-butene (Cares and Hightower, 1971; Kung *et al.*, 1981). The reverse step of the homolysis created the isomers and lowered the selectivity of BD. In this case, it is reasonable to expect higher isomer selectivity in the reactions of cis-2-butene. On the other hand, the ODH process of butenes on $Co_9Fe_3Bi_1Mo_{12}O_{51}$ follows a mechanism involving the formation of a carbocation, which for 2-butenes requires higher energy consumption (Zhang *et al.*, 1985). Thus, a lower selectivity of BD would be expected in the ODH of 2-butenes on $Co_9Fe_3Bi_1Mo_{12}O_{51}$. In the dual bed system, the isomers created by the first bed could still be converted more efficiently in the second bed. Packing $ZnFe_2O_4$ on top could lead to a higher conversion of 2-butenes, and the $Co_9Fe_3Bi_1Mo_{12}O_{51}$ in the second bed could convert the resulting 1-butene with higher activity. This effect would lead to a higher selectivity of BD, especially when $ZnFe_2O_4$ was on top of the bed.

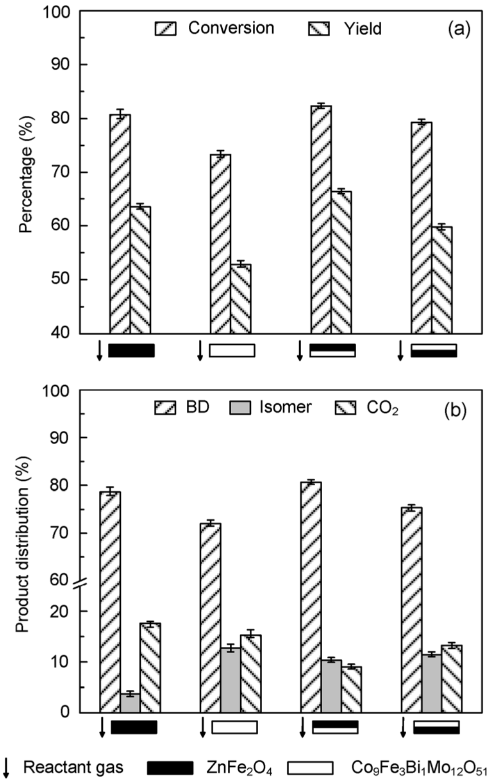

Fig. 3 ODH of trans-2-butene over different catalyst systems

(a) Conversion of 1-butene and yield of BD; (b) Product distribution of BD, butene isomers, and CO_2. Reaction conditions: butene/oxygen/steam=1/0.82/10.4; reaction temperature is 375 °C; GHSV is 438 h^{-1} on the basis of butene

3.3 Performance of individual and dual bed catalyst systems in ODH of mixed-butenes

Fig. 5 gives the performance of different catalyst systems in the ODH of mixed-butenes. The conversion of 2-butenes on $ZnFe_2O_4$ was higher than that on $Co_9Fe_3Bi_1Mo_{12}O_{51}$. Although $Co_9Fe_3Bi_1Mo_{12}O_{51}$ showed a better conversion of 1-butene and a higher BD selectivity, a lower BD yield was observed due to its lower catalytic activity toward 2-butenes.

Compared with the single bed systems, the dual bed systems showed better conversion of the mixed-butenes. Specifically, packing $ZnFe_2O_4$ on the top had a higher conversion of 2-butenes, while the conversion of 1-butene also increased due to the better catalytic performance of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ in the second bed. The same mechanism could be applied to the other dual bed system. Furthermore, similar BD selectivity was observed on both dual bed systems, indicating an overall higher mixed-butene amount in the ODH reaction. Overall, packing $ZnFe_2O_4$ on the top resulted in a higher conversion of mixed-butenes, which eventually led to a higher yield of BD.

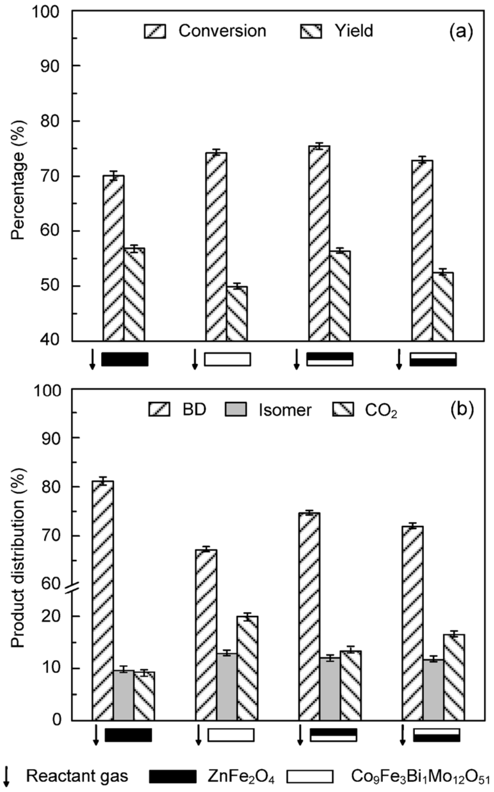

Fig. 4 ODH of cis-2-butene over different catalyst systems
(a) Conversion of 1-butene and yield of BD; (b) Product distribution of BD, butene isomers, and CO_2. Reaction conditions: butene/oxygen/steam=1/0.82/10.4; reaction temperature is 375 °C; GHSV is 438 h^{-1} on the basis of butene

3.4 Synergistic effect

The above results indicate that the existence of butene isomers in mixed-butenes can lead to an increase in overall conversion of butene in dual bed catalyst systems. Thus, the effect of butene composition and the catalyst packing sequence on conversion was investigated to explore the intrinsic mechanism (Fig. 6).

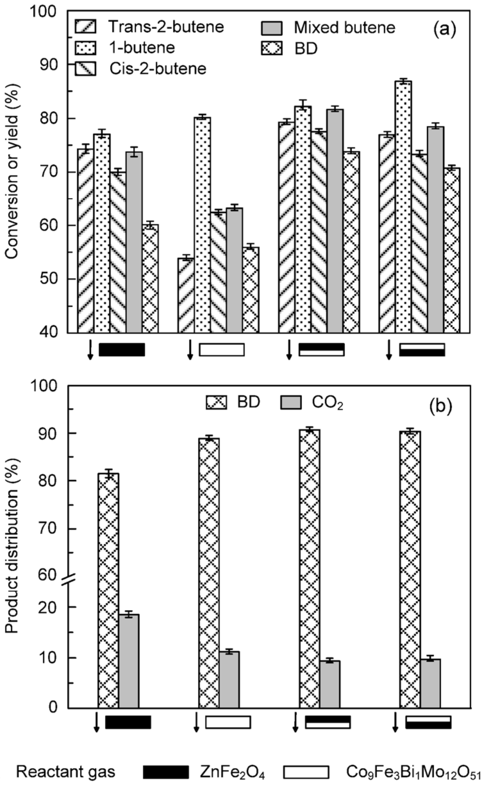

Fig. 5 ODH of mixed-butenes over different catalyst systems
(a) Conversion of butene isomers and yield of BD; (b) Product distribution of BD and CO_2. Reaction conditions: butene/oxygen/steam=1/0.82/10.4; reaction temperature is 375 °C; GHSV is 438 h^{-1} on the basis of butene; the ratio of butene isomers in the initial feed was maintained at 1-butene/trans-2-butene/cis-2-butene=6.5/11.2/8.3

In the dual bed catalyst system, the conversion of each butene isomer was improved in the ODH of mixed-butenes, compared with that in their individual ODH reactions. The increase of each butene isomer conversion would lead finally to increased mixed-butene conversion as well as increased BD yield. Thus, we proposed a mechanism for the synergistic effect within this dual bed catalyst system. As stated, $ZnFe_2O_4$ and $Co_9Fe_3Bi_1Mo_{12}O_{51}$ show different catalytic performance toward different butene isomers. As the reactant passes through $ZnFe_2O_4$, there would be a higher conversion of the favored trans-2-butene and cis-2-butene. The result would be a lowered proportion of those but a higher proportion of 1-butene in the feed. Coincidentally, the $Co_9Fe_3Bi_1Mo_{12}O_{51}$ catalyst packed in the second bed favors the ODH of 1-butene. The changed proportion

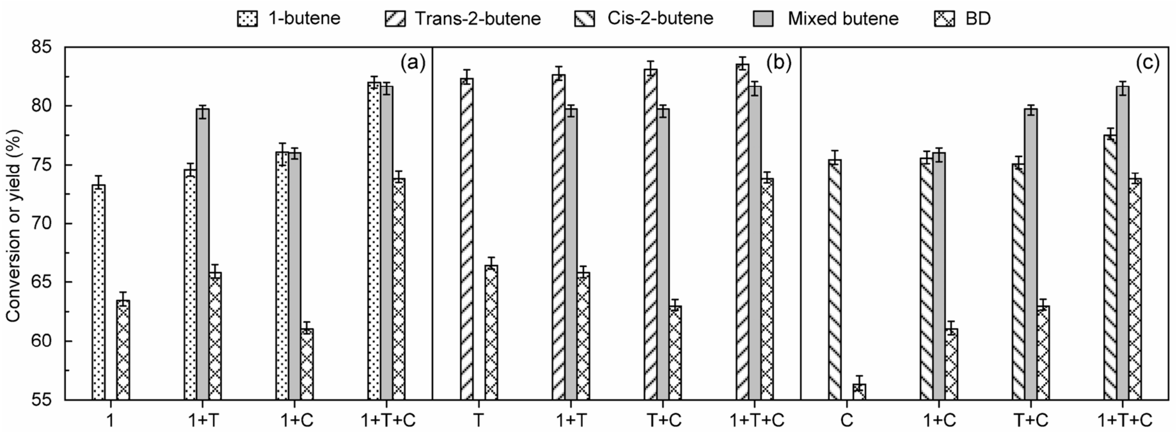

Fig. 6 Influence of butene isomer on mixed-butene conversion: (a) 1-butene; (b) trans-2-butene; (c) cis-2-butene

1 represents 1-butene; T represents trans-2-butene; C represents cis-2-butene. Reaction conditions: butene/oxygen/steam= 1/0.82/10.4; reaction temperature is 375 °C; GHSV is 438 h^{-1} on the basis of butene; the ratio of isomers in the initial feed was maintained at 1-butene/trans-2-butene/cis-2-butene=6.5/11.2/8.3 when adding different isomers to the system; the catalyst bed was formed by packing $ZnFe_2O_4$ on the top and $Co_9Fe_3Bi_1Mo_{12}O_{51}$ on the bottom

of butene isomers between the catalyst beds would enhance the catalytic performance of the second bed, leading to higher conversions of all butene isomers. On the other hand, the presence of all butene isomers would inhibit their isomerization to a certain degree. This inhibition could result in a higher proportion of mixed-butenes in the ODH reactions, for its highest reaction rate in the system (Zhang *et al.*, 1992). The above effects would contribute to a higher conversion of each butene isomer, and finally the increased BD yield.

Comparative experiments were conducted to prove such a mechanism. The results of mixed feeds consisting of two butene isomers were compared with those of single and mixed-butenes. The conversion of 1-butene and mixed-butenes increased as the feed changed with the addition of either trans-2-butene or cis-2-butene (Fig. 6a). Similar results are also shown in Figs. 6b and 6c. The increased conversion of each butene isomer confirmed the enhanced catalytic performance of the second bed. The increased BD yield also indicated the increased proportion of ODH reaction in the system (Fig. 6c). These comparisons provide solid evidence in support of the proposed mechanism of the synergistic effect.

Note that the isomerization process follows the rules of thermodynamic equilibrium. The changed composition of butene isomers could affect only the final concentration of the butene isomers. The equilibrium constant remained the same because the reaction temperature was kept constant.

3.5 Packing volume optimization in different packing sequences

Fig. 7 illustrates the optimization of the catalyst packing volume in the bed and the correlation between packing volume and catalytic performance. Both packing sequences tested showed that the dual bed catalyst systems exhibited better catalytic performance than single catalysts. As the catalyst packing volume ratio changed, the conversion of butene isomers underwent an initial increase followed by a decrease (Figs. 7a and 7c). In Figs. 7b and 7d, the BD yield shows the same tendency.

The mixed-butene conversion increased as the packing ratio approached 5/5 (Fig. 7a). The conversion of 1-butene remained relatively constant, while those of both trans-2-butene and cis-2-butene increased with increasing amounts of $ZnFe_2O_4$. The conversion of mixed-butenes was relatively high when the packing volume ratio of $ZnFe_2O_4$ and $Co_9Fe_3Bi_1Mo_{12}O_{51}$ was kept between 6/4 and 4/6. In Fig. 7c, the change in conversion is relatively mild, but the highest conversion is still found at a ratio of 4/6. The 1-butene conversion increased dramatically as the volume of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ increased above 60% in the dual bed catalyst system.

In Fig. 7b, the packing ratios showing high catalytic performance were between 4/6 and 6/4. Further

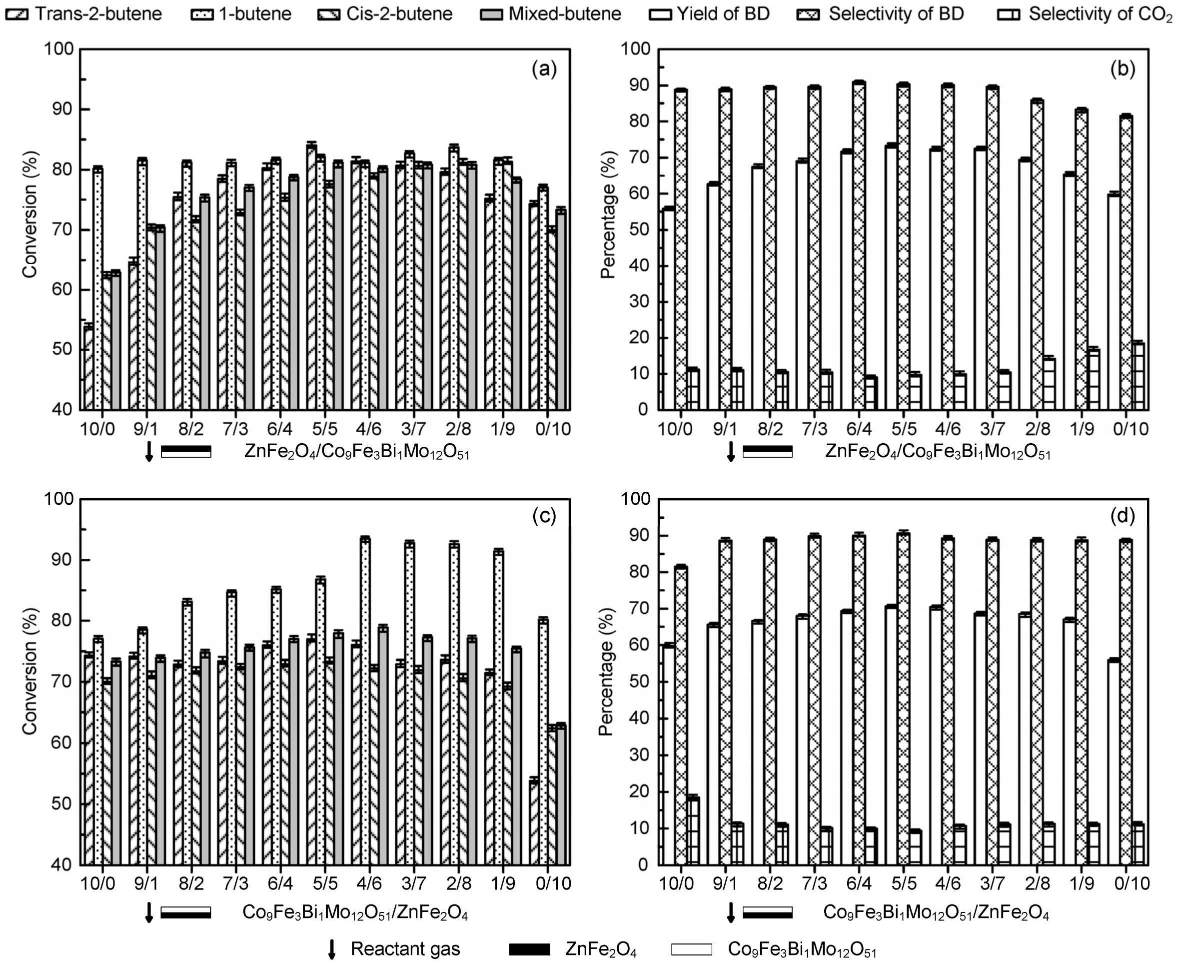

Fig. 7 Packing volume optimization in the dual bed catalyst system

(a) & (c): Conversion of three butene isomers and total conversion; (b) & (d): Selectivity of products and yield of 1,3-butadiene; (a) & (b): Packing $ZnFe_2O_4$ on top; (c) & (d): Packing $Co_9Fe_3Bi_1Mo_{12}O_{51}$ on top. Reaction conditions: butene/oxygen/steam=1/0.82/10.4; reaction temperature is 375 °C; GHSV is 438 h^{-1} on the basis of butene; the ratio of isomers in the initial feed was maintained at 1-butene/trans-2-butene/cis-2-butene=6.5/11.2/8.3

increases in the volume of $Co_9Fe_3Bi_1Mo_{12}O_{51}$ would lead to increasing CO_2 selectivity. In Fig. 7d, the BD selectivity is higher than that in Fig. 7b. This result would compensate for the lower conversion over this packing sequence. A high yield was achieved when the packing ratios were between 7/3 and 3/7. However, the highest yields of the two packing sequences were rather close, with packing $ZnFe_2O_4$ on top being slightly better than $Co_9Fe_3Bi_1Mo_{12}O_{51}$ on top (73.3% versus 70.7%, respectively).

In summary, packing ratios between 4/6 and 6/4 where $ZnFe_2O_4$ was packed on the top gave better results in terms of BD yield. This also provided further proof for the existence of the synergistic effect.

4 Conclusions

$ZnFe_2O_4$ showed better catalytic performance in ODH of both trans-2-butene and cis-2-butene, while $Co_9Fe_3Bi_1Mo_{12}O_{51}$ showed a better catalytic activity over 1-butene. The dual bed catalytic system gave a better catalytic performance than either individual catalyst alone. A synergistic effect of the dual bed system was proposed based on the increased conversion of mixed-butenes resulting from the redistribution of butene isomers between the catalyst beds. The redistribution makes use of the advantages in both catalyst beds. Also, as all butene isomers were included in the feed, the suppression of isomerization would be enforced. The ODH reaction became a more predominant reaction in the system, leading to the improved overall conversion of mixed-butenes. A series of experiments involving different mixed-butene compositions were conducted to prove the above mechanism. Further optimization of this catalytic system revealed that loading $ZnFe_2O_4$ on top while maintaining the volume ratio between 4/6 and 6/4 led to better overall conversion and increased BD yield. The optimized results provide instructive information for the production of a composite catalyst for the ODH of mixed-butenes.

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中文概要

题　目： 混合丁烯氧化脱氢双层床催化剂体系的协同作用机理

目　的： 通过对混合丁烯氧化脱氢过程进行反应表征，对由 ZnFe$_2$O$_4$和 Co$_9$Bi$_1$Fe$_3$Mo$_{12}$O$_{51}$组成的双床层催化剂体系中存在的协同机理进行解释；将异构化反应过程纳入反应体系，得出混合丁烯转化率和丁二烯收率上升的原因。

创新点： 1. 提出基于丁烯异构体在床层之间浓度重分布和异构化效应抑制作用的协同作用机理；2. 设计验证实验，从直观角度证实机理，并优化了催化剂的装填量和装填顺序。

方　法： 1. 通过单一丁烯和混合丁烯的氧化脱氢反应，对单一催化剂和双床层催化剂进行反应评估，得到相关反应数据；2. 通过设计对比实验，从改变参加反应物质的直观角度对协同机理进行验证和解释；3. 对参加反应的双层床催化剂中两种催化剂的装填量和装填顺序进行优化，为进一步研究组合型催化剂提供实验基础。

结　论： 1. ZnFe$_2$O$_4$对两种 2-丁烯有更优的催化效果，而 Co$_9$Bi$_1$Fe$_3$Mo$_{12}$O$_{51}$对 1-丁烯有更优的催化效果，由两者组成的双层床催化体系对单一丁烯和混合丁烯的反应效果都有所提升，证明两种催化剂之间存在协同效应。2. 双层床催化剂体系中，两种催化剂之间的协同作用机理是：催化剂不同活性导致丁烯异构体在床层之间的浓度发生重分布，同时由于多种异构体同时存在抑制了异构化反应。3. 对双层床催化剂体系的装填顺序和装填量的优化结果表明，ZnFe$_2$O$_4$ 装填在上层，Co$_9$Bi$_1$Fe$_3$Mo$_{12}$O$_{51}$ 装填在下层，且两者比例处于 4:6 到 6:4 之间时催化效果最佳。

关键词： 混合丁烯；氧化脱氢；双层床催化剂体系；协同作用