

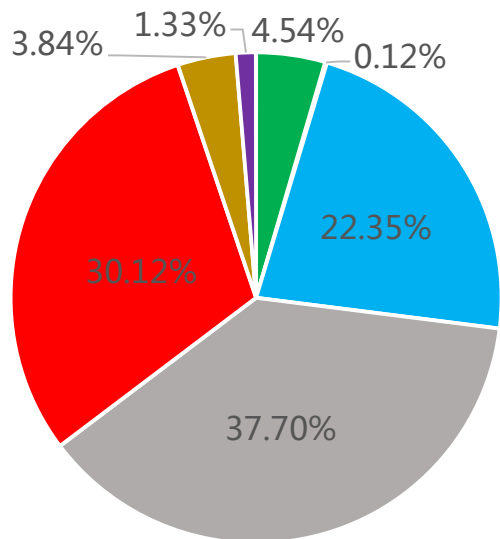
## Dual bed catalyst system for oxidative dehydrogenation of mixed-butenes: a synergistic mechanism

Xiao-yi Li, Dang-guo Cheng, Feng-qiu Chen, Xiao-li Zhan

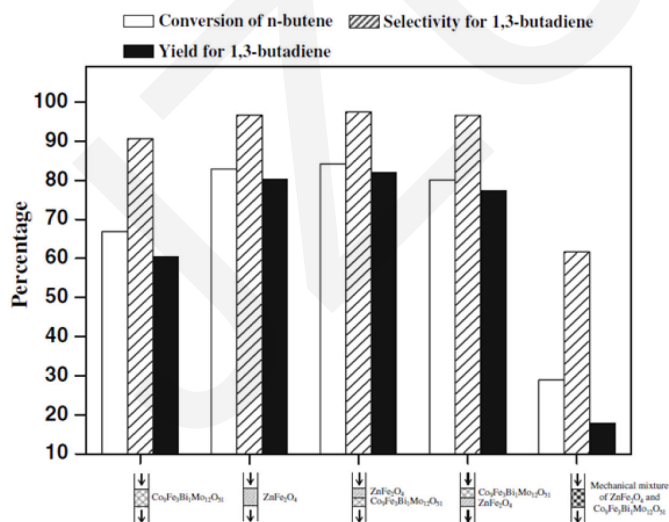
Cite this as: Xiao-yi Li, Dang-guo Cheng, Feng-qiu Chen, Xiao-li Zhan, 2017. Dual bed catalyst system for oxidative dehydrogenation of mixed-butenes: a synergistic mechanism. *Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering)*, 18(3):225-233.

<http://dx.doi.org/10.1631/jzus.A1600295>

# Background

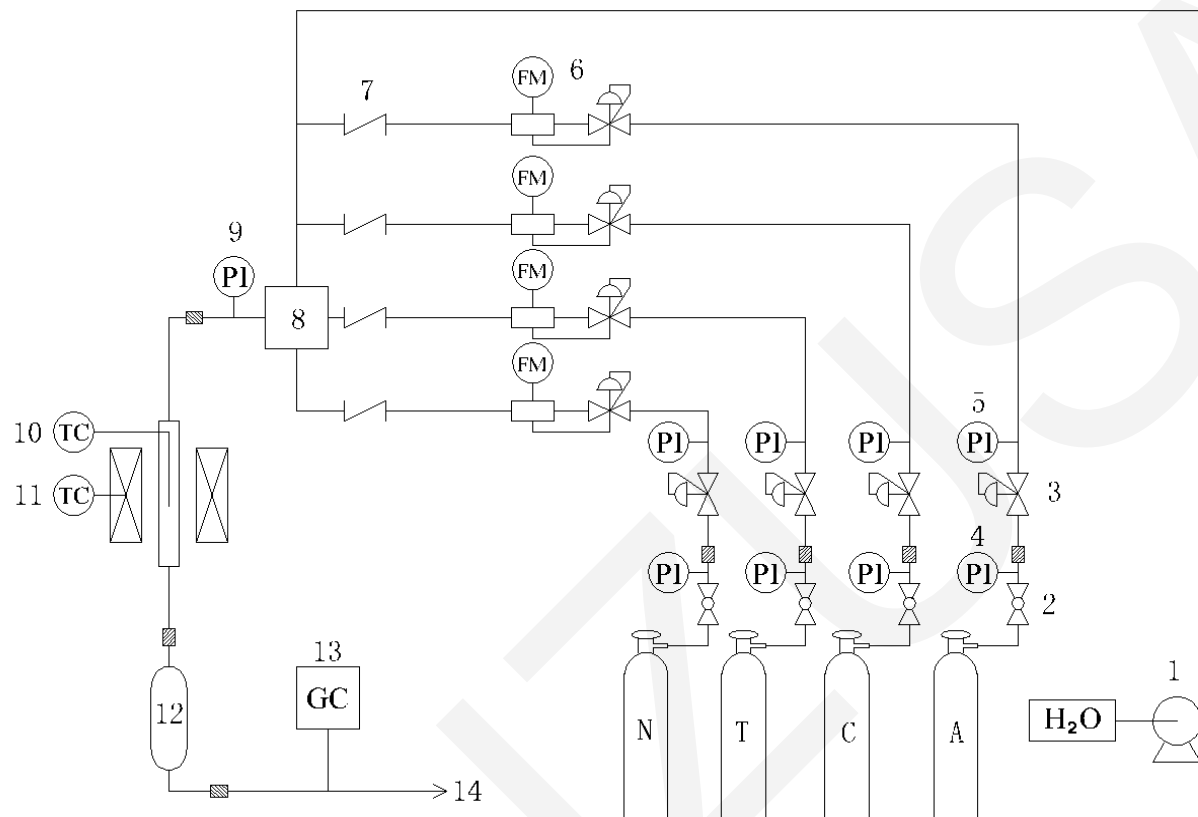


- Butane
- Isobutane
- 1-Butene
- Tran-2-butene
- Cis-2-butene
- Isobutene
- 1,3-Butadiene



**Efficient utilization of C4 resources via oxidative dehydrogenation**

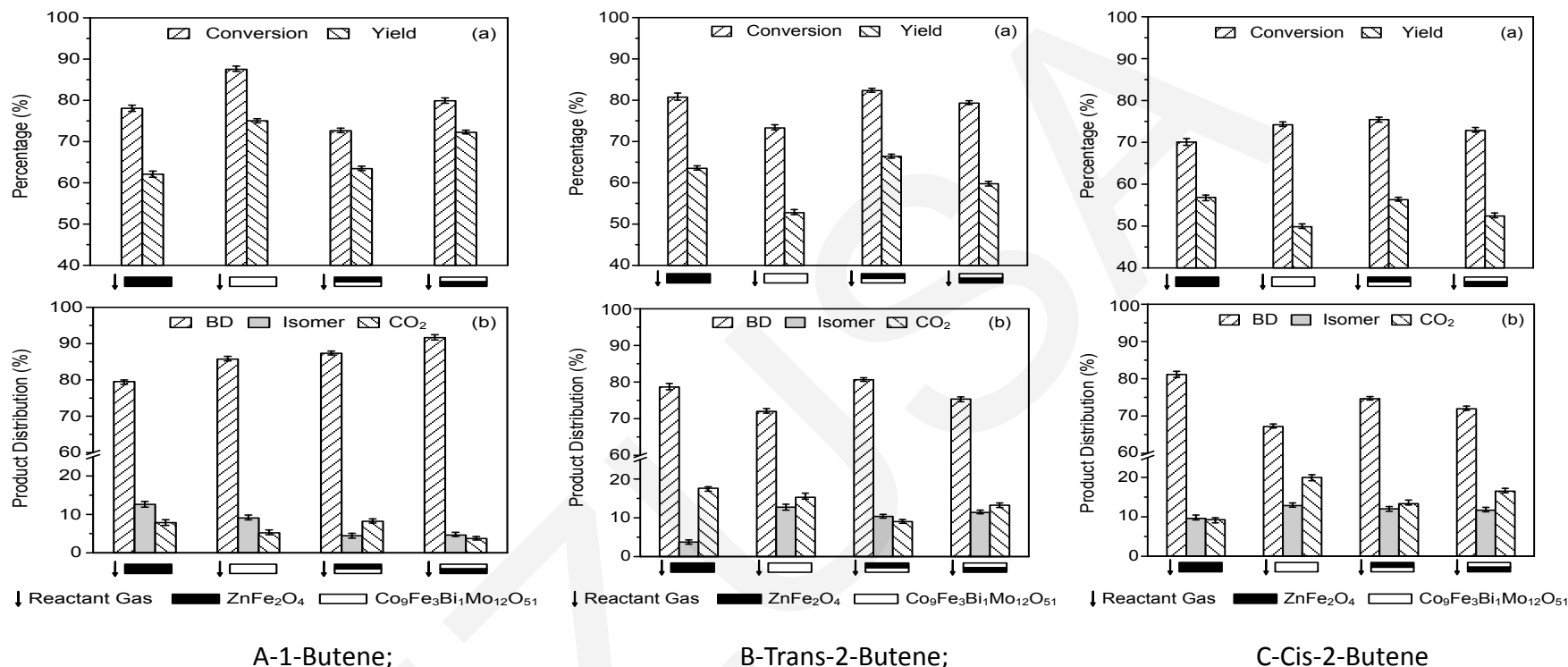
[1] J. C. Jung *et al.*, *Catal Lett* (2008) 123: 239–245



ODH reaction was carried out in a fixed-bed reactor.  
N: 1-butene; T: Trans-2-butene; C: Cis-2-butene;  
A: Air

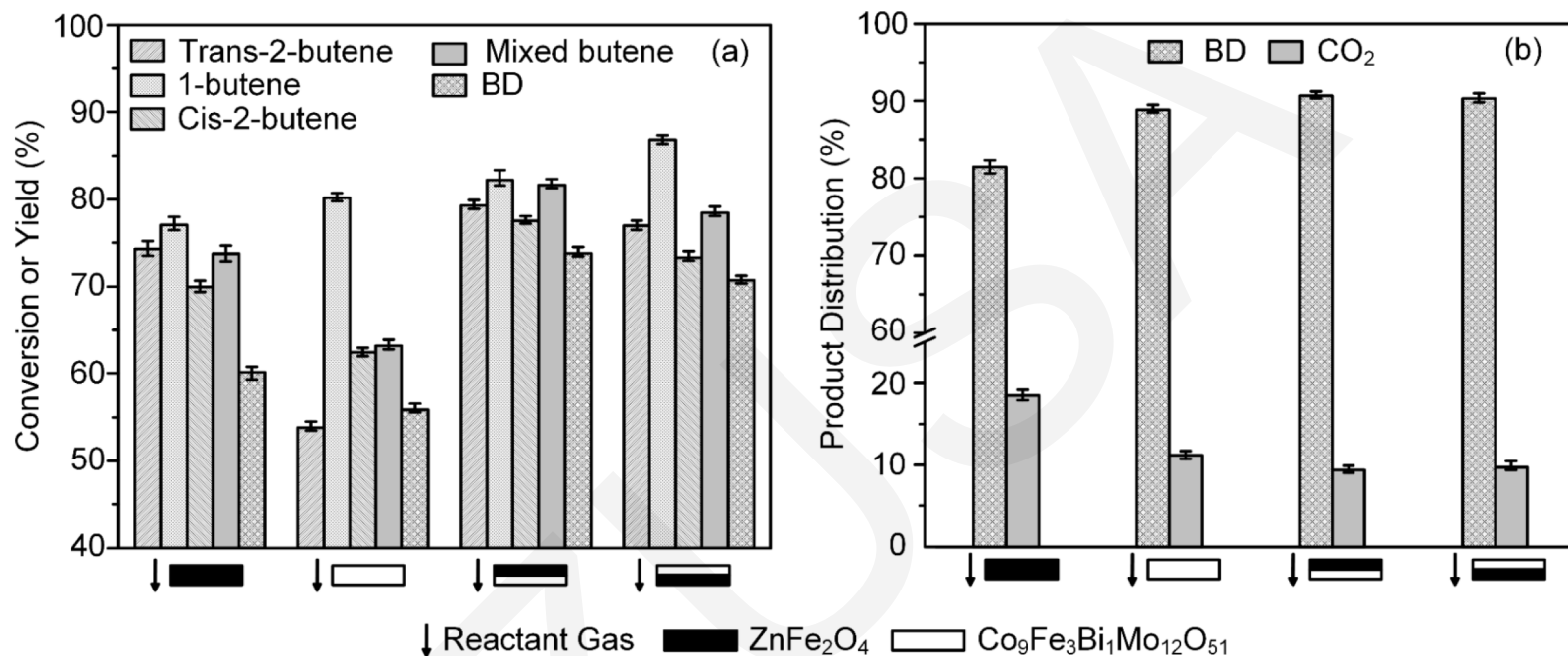
Butene/Oxygen/Steam = 1/0.82/10.4; Reaction temperature: 375 °C;  
GHSV: 438 h<sup>-1</sup> on the basis of butene.

# Performance in ODH of butene isomers



ZnFe<sub>2</sub>O<sub>4</sub> showed better catalytic performance in ODH of both trans-2-butene and cis-2-butene, while Co<sub>9</sub>Fe<sub>3</sub>Bi<sub>1</sub>Mo<sub>12</sub>O<sub>51</sub> showed a better catalytic activity over 1-butene. The dual bed catalytic system gave a better catalytic performance than either individual catalyst alone.

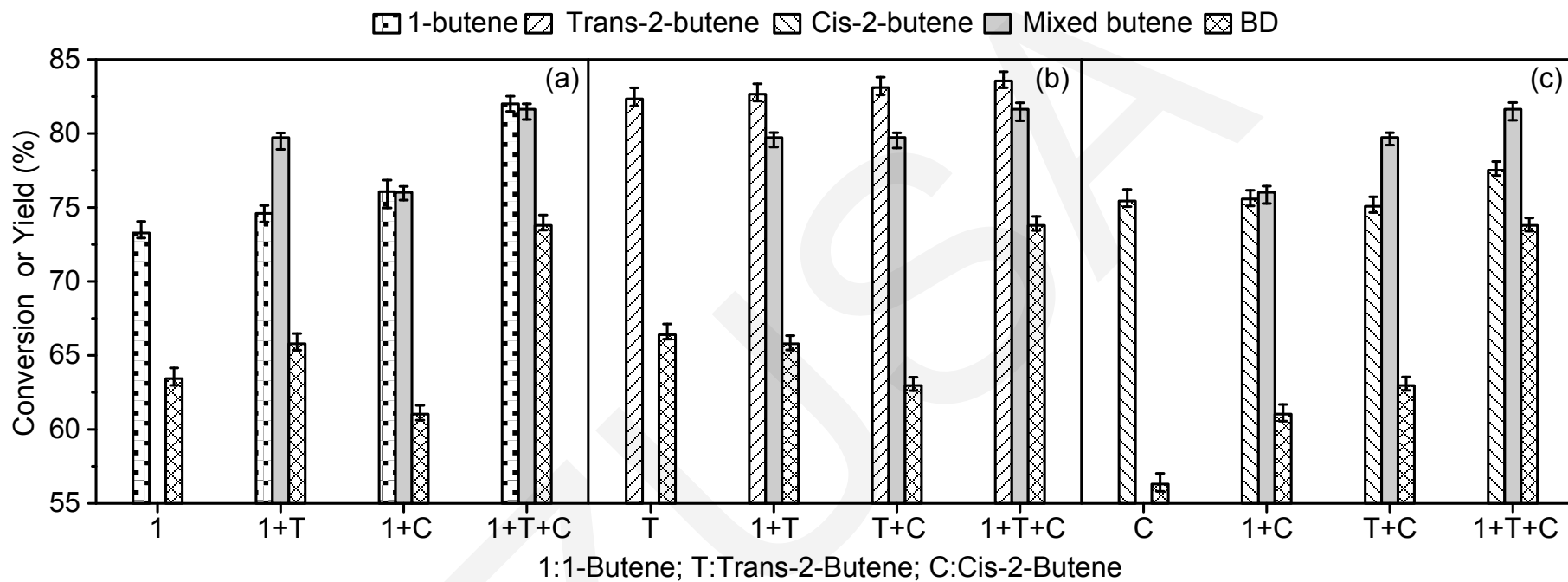
# Performance in ODH of mixed-butenes



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.

A higher conversion of all butene isomers were obtained with targeted catalyst beds and a similar BD selectivity was observed on both dual bed systems, indicating an overall higher conversion.

# The synergistic effect

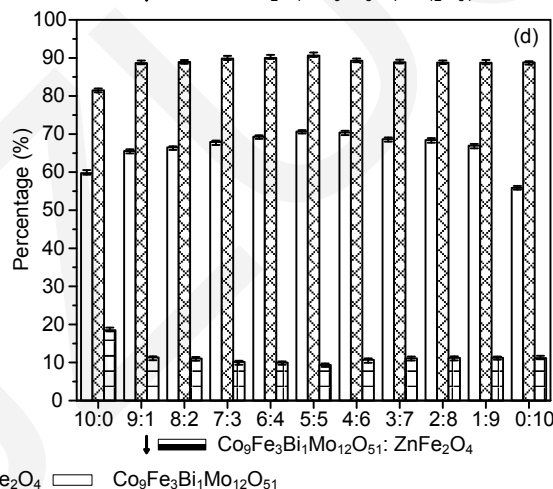
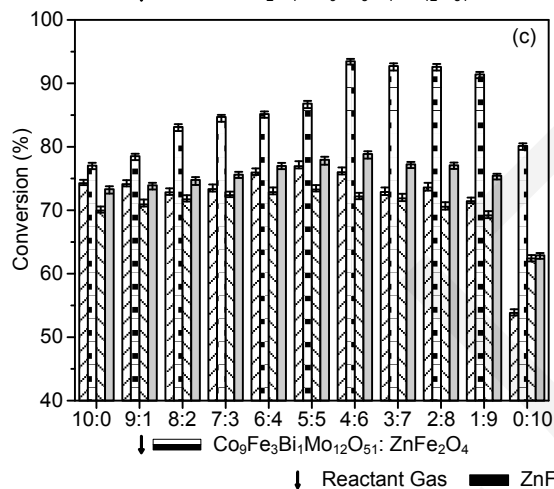
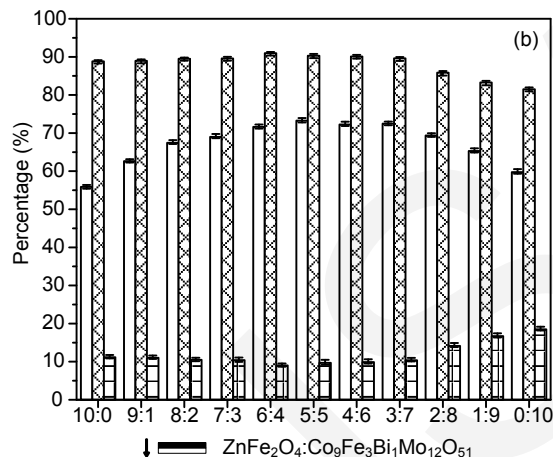
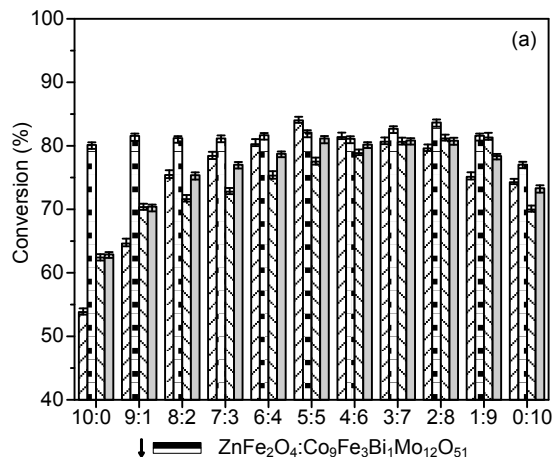


1-butene/trans-2-butene/cis-2-butene = 6.5/11.2/8.3. The catalyst bed was formed by packing  $\text{ZnFe}_2\text{O}_4$  on top and  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$  on the bottom. Influence of butene isomer addition to the system on the conversion of (a) 1-butene, (b) trans-2-butene and (c) cis-2-butene

Different catalytic performance of  $\text{ZnFe}_2\text{O}_4$  and  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$  toward different butene isomers contributed to a higher conversion of butenes favored by the second bed. Additionally, the isomerization was inhibited, resulting in a higher conversion rate of mixed butenes in the system.

# Packing volume optimization

  Trans-2-Butene 
   1-Butene 
   Cis-2-Butene 
   Mixed-Butene 
   Yield of BD 
   Selectivity of BD 
   Selectivity of CO<sub>2</sub>



Packing ratios between 4:6 and 6:4 where ZnFe<sub>2</sub>O<sub>4</sub> was packed on the top gave better results in terms of BD yield.

1-butene/trans-2-butene/cis-2-butene = 6.5/11.2/8.3.

- I.  $\text{ZnFe}_2\text{O}_4$  showed better catalytic performance in ODH of both trans-2-butene and cis-2-butene, while  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$  showed a better catalytic activity over 1-butene. The dual bed catalytic system gave a better catalytic performance than either individual catalyst alone.
- II. A higher conversion of all butene isomers were obtained with targeted catalyst beds and a similar BD selectivity was observed on both dual bed systems, indicating an overall higher conversion.
- III. Different catalytic performance of  $\text{ZnFe}_2\text{O}_4$  and  $\text{Co}_9\text{Fe}_3\text{Bi}_1\text{Mo}_{12}\text{O}_{51}$  toward different butene isomers contributed to a higher conversion of butenes favored by the second bed. Additionally, the isomerization was inhibited, resulting in a higher conversion rate of mixed butenes in the system.
- IV. Packing ratios between 4:6 and 6:4 where  $\text{ZnFe}_2\text{O}_4$  was packed on the top gave better results in terms of BD yield.

# Relevant Published Papers

1. Xiaoyi Li, Dang-guo Cheng Zhi-Jian Zhao, Fengqiu Chen, Jinlong Gong. Temperature-induced Deactivation Mechanism of  $\text{ZnFe}_2\text{O}_4$  for Oxidative Dehydrogenation of 1-Butene, *React. Chem. Eng.*, 2017, Advance Article, Doi: 10.1039/C6RE00179C
2. Xiaoyi Li, Dangguo Cheng, Fengqiu Chen, Xiaoli Zhan, Controllable modification of mesoporous carbon and its performance in oxidative dehydrogenation of 1-butene, *Chem. React. Eng. Technol.*, 2016 Vol. 32 (6): 513-521