Journal of Zhejiang University – Science A

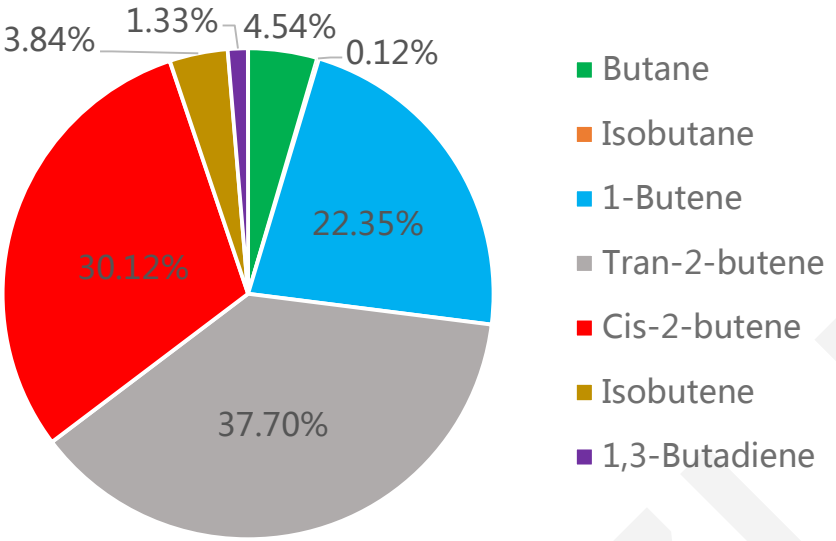
Dual bed catalyst system for oxidative dehydrogenation of mixed-butenes: a synergistic mechanism

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

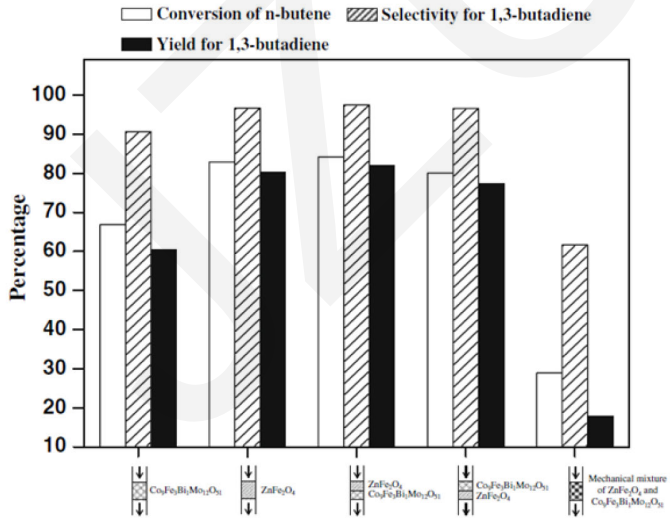
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Background





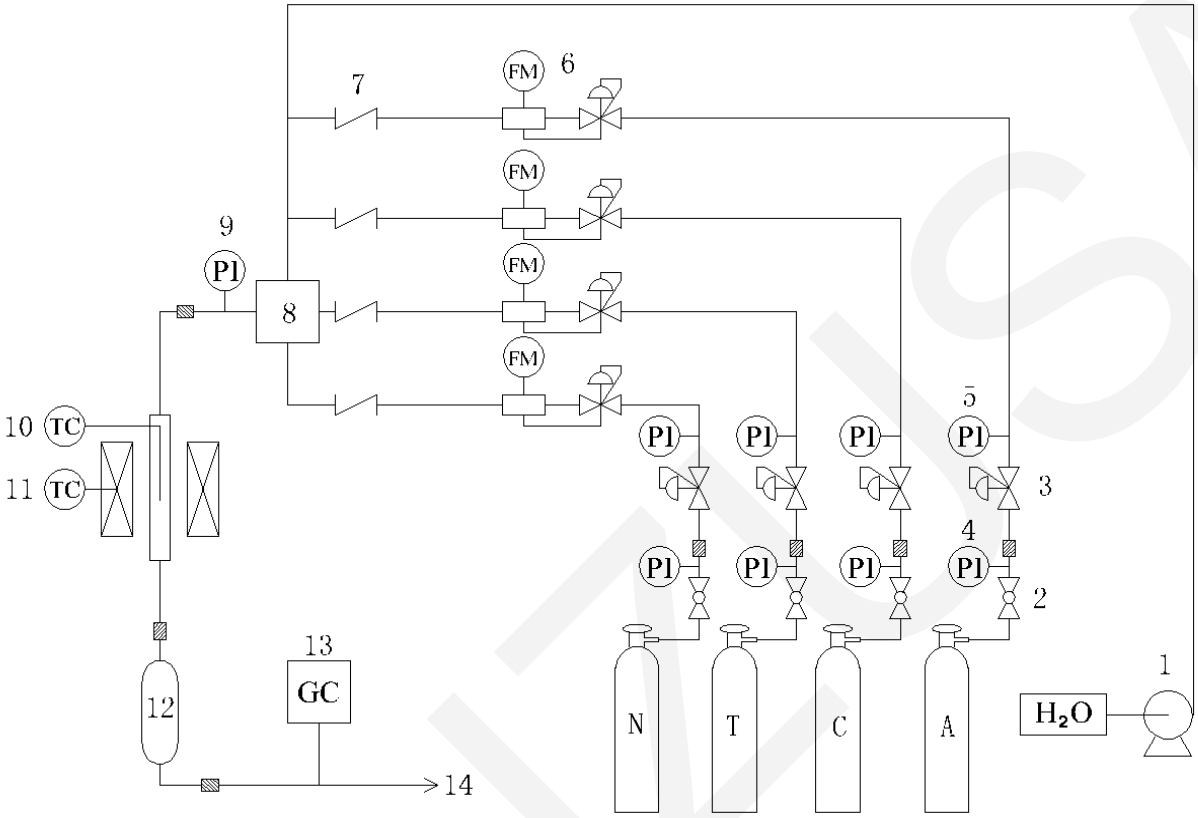


Efficient utilization of C4 resources via oxidative dehydrogenation

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

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Methods

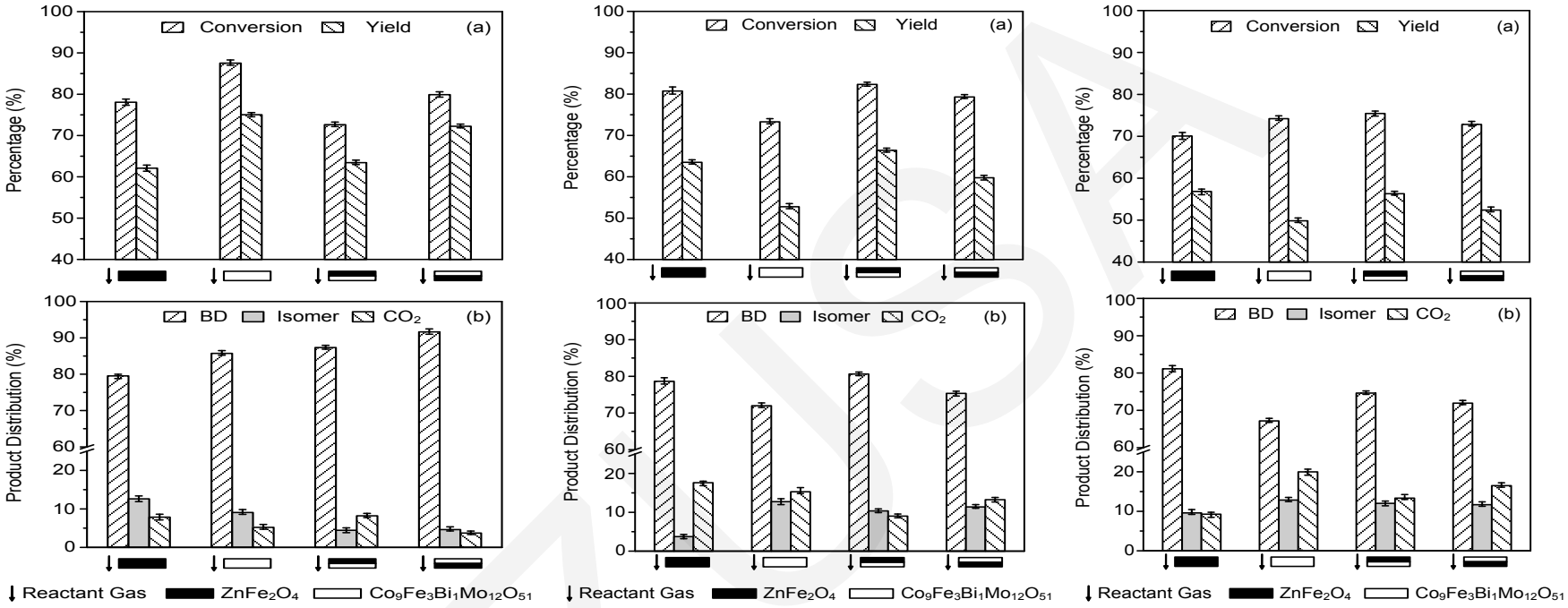


ODH reaction was carried out in a fixed-bed reactor. N: 1-butene; T: Trans-2-butene; C: Cis-2-butene; A: Air

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

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Performance in ODH of butene isomers

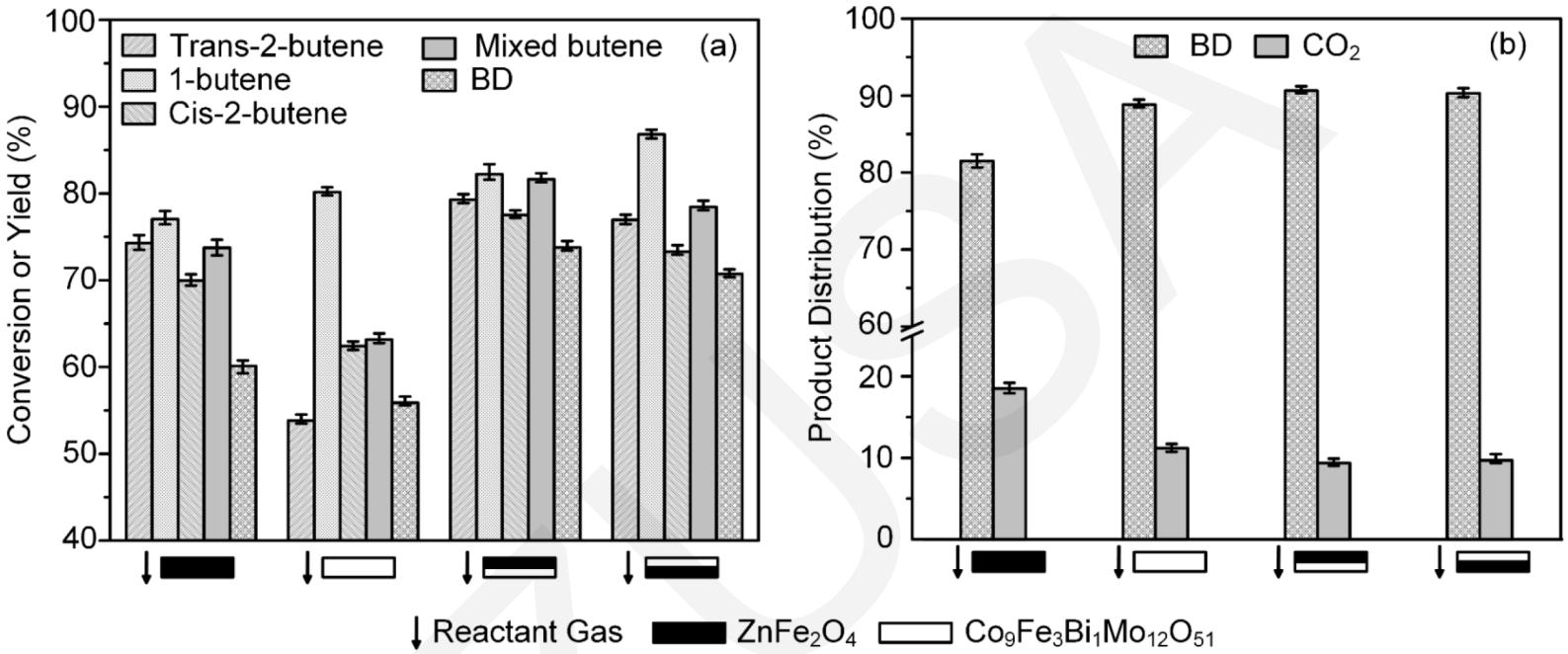


A-1-Butene; B-Trans-2-Butene; C-Cis-2-Butene

$ZnFe_2O_4$ 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.

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Performance in ODH of mixed-butenes

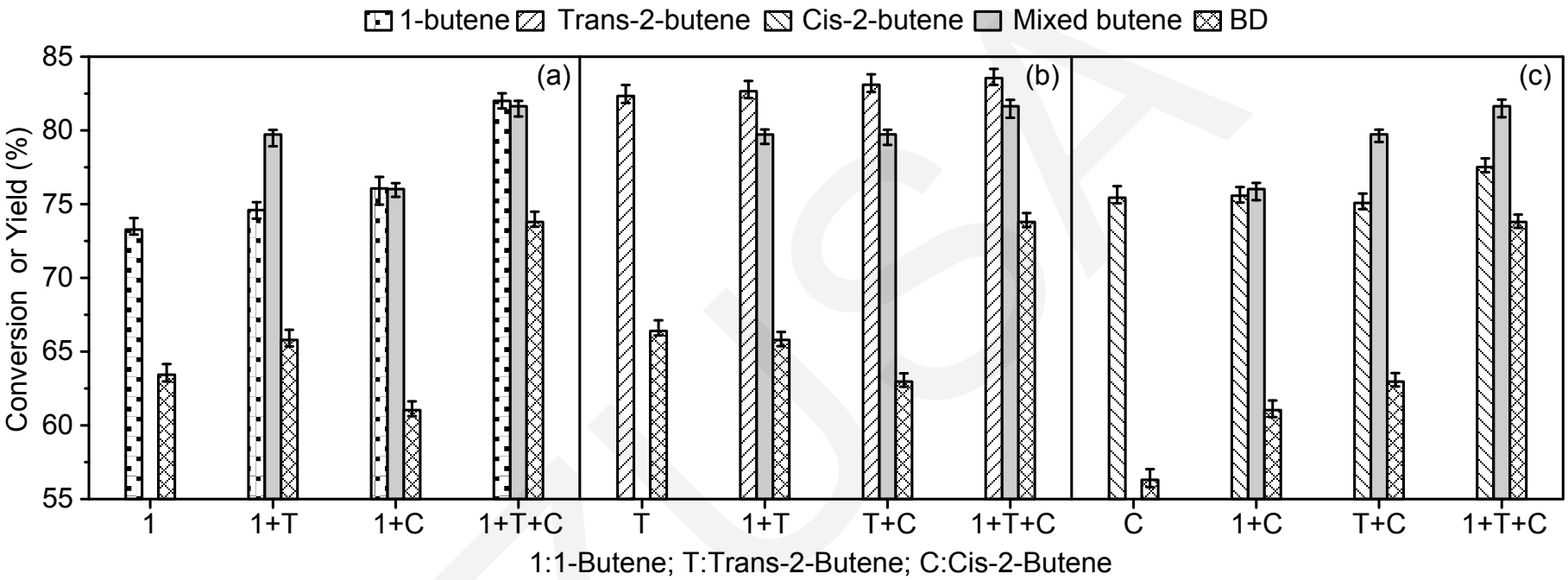


The ratio of butene isomers in the initial feed was maintained at 1-butene/trans-2-butene/cis-2-butene = 6.5/11.2/8.3.

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.

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The synergistic effect

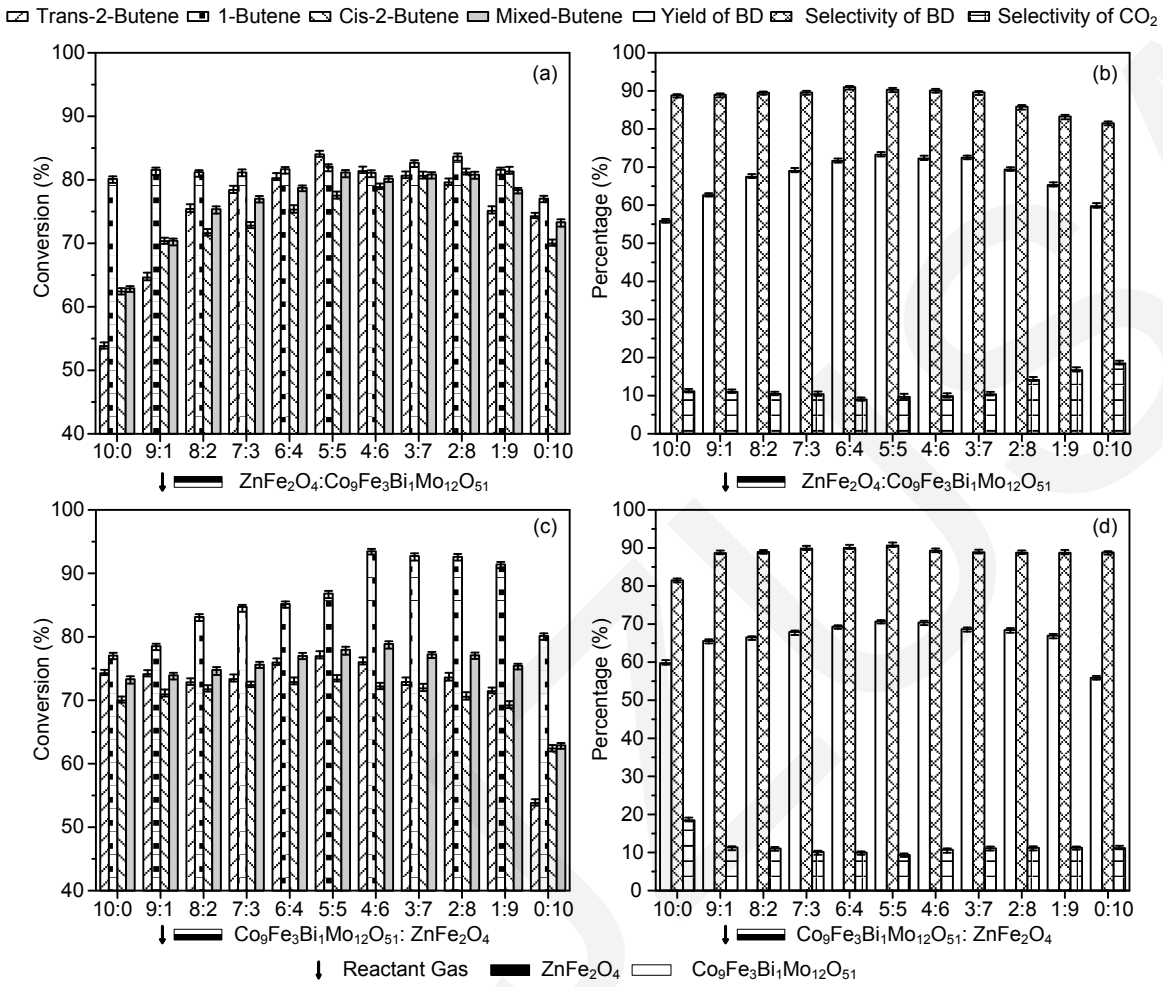


1-butene/trans-2-butene/cis-2-butene = 6.5/11.2/8.3. The catalyst bed was formed by packing $ZnFe_2O_4$ on top and $Co_9Fe_3Bi_1Mo_{12}O_{51}$ on the bottom. Influence of butene isomer addition to the system on the conversion of (a) 1-butene, (b) trans-2-butene and (c) cis-2-butene

Different catalytic performance of $ZnFe_2O_4$ and $Co_9Fe_3Bi1Mo_{12}O_{51}$ toward different butene isomers contributed to a higher conversion of butenes favored by the second bed Additionally, the isomerization was inhibited, resulted in a higher conversion rate of mixed butenes in the system

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Packing volume optimization



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.

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

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Conclusions

I. $ZnFe_2O_4$ 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.

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 $ZnFe_2O_4$ and $Co_9Fe_3Bi1Mo_{12}O_{51}$ toward different butene isomers contributed to a higher conversion of butenes favored by the second bed Additionally, the isomerization was inhibited, resulted in a higher conversion rate of mixed butenes in the system

IV. 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.

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Relevant Published Papers

1. Xiaoyi Li, Dang-guo Cheng Zhi-Jian Zhao, Fengqiu Chen, Jinlong Gong. Temperature-induced Deactivation Mechanism of $ZnFe_2O_4$ 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

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