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Metathesis of C_4 olefin over Mo-based heterogeneous catalysts: A novel route to propene and isopentene

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ABSTRACT

A novel route with high yields of propene and isopentene on the basis of consecutive metathesis of 1-butene and isobutene is proposed. Two series of Mo-based catalysts supported on γ-Al_2O_3 and HMOR-Al_2O_3 composite materials were prepared and evaluated in a fixed bed reactor. Experimental results revealed that three interesting reactions occurred on the catalysts, i.e. 1-$C_4^=$ → 2-$C_4^=$ (Isomerization I), 2-$C_4^=$ + 1-$C_4^=$ → $C_3^=$ + 2-$C_5^=$ (Metathesis I), 2-$C_4^=$ + *i*-$C_4^=$ → $C_3^=$ + *i*-$C_5^=$ (Metathesis II). Isomerization I was the prerequisite step of the following two metathesis reactions. Metathesis I was more acidity-sensitive and it could happen at low temperatures provided that the catalyst acidity was sufficient. Metathesis II, as the targeted reaction, was proved to be more temperature-sensitive, and high reaction temperatures were preferable for the metathesis of 2-butene and isobutene. $6Mo/Al_2O_3$ exhibited the best catalytic metathesis performance among the candidate catalysts in the consecutive metathesis of 1-butene and isobutene. Furthermore, isopentene selectivity could be highly enhanced through the steam treatment of γ-Al_2O_3 support. The modifications of alumina support led to the different distribution of Mo species and the formation of more Mo species in octahedral state may contribute to the preferential activation of Metathesis II.

1. Introduction

Propene is an important industrial chemical intermediate that serves as one of the building blocks for an array of chemical and plastic products. The demand for propene is growing rapidly in worldwide chemistry and new processes with high yield of propene are urgently required. Several on-purpose propene production technologies, including propane dehydrogenation [1,2], catalytic cracking of C_4^+ olefins [3,4] and methanol to olefin process [5], are available. In addition, another promising technology is olefin metathesis reaction [6,7], of which the C_4 olefin feed could be 1-butene or 2-butene.

Olefin metathesis is a powerful carbon skeleton rearrangement reaction in which the unsaturated carbon–carbon bonds can be redistributed in the presence of catalysts [8]. Since its discovery in 1964, much effort has been devoted to the design of homogeneous organic catalysts [9,10]. Heterogeneous catalysts, due to their virtue of easy separation, good persistence and recyclability, are of particular interest for both academic and industrial researchers. Among them, molybdenum oxide supported on alumina [11,12], siliceous materials [13], silica–alumina [14–16] and zeolite–alumina composite supports [17,18] have received great interest because of their relatively low price and high activity under mild reaction conditions.

So far, several olefin metathesis reaction routes have been developed to increase the propene output, such as cross-metathesis of ethene and 2-butene [6,7,19], auto-metathesis of 1-butene [17,20–22] and metathesis of 2-butene [23]. The above-mentioned processes either consume valuable ethene source or require the separation of C_4 olefin streams. New metathesis pathways based on the direct utilization of mixed C_4 olefin stream would be more popular for the production of value-added propene. C_4 olefin stream is usually the by-product of steam cracker and FCC units. Among them, isobutene component could be further manufactured as the additive of gasoline or polymer materials, while much of the other components in the C_4 olefin are used as fuel in China. Metathesis of 2-butene (1-butene) and isobutene provides an alternative way to produce propene and isopentene. It could make full use of the surplus C_4 olefin stream directly without further separation, and provide an alternative route for isobutene utilization. On the other hand, isopentene is obtained simultaneously with propene which is also an important intermediate in petrochemical industry and could be used to produce *tert*-amyl methyl ether (TAME) and isoprene. Generally, isopentene and isoprene are obtained from

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