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Comparison of physically mixed and separated MgO and WO_3/SiO_2 catalyst for propylene production via 1-butene metathesis

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Abstract−We examined the catalyst bed design of MgO and WO_3/SiO_2 for production of propylene via metathesis of 1-butene. WO_3/SiO_2 was used as a bi-functional catalyst for isomerization and metathesis reactions. Addition of MgO was proposed to help improve the isomerization activity and hence the propylene yield. Experimental studies were carried out to determine activity and reaction kinetics of 1-butene isomerization over MgO isomerization catalyst and 1-butene metathesis over WO_3/SiO_2 bi-functional catalyst for designing a suitable catalyst bed. Two types of catalyst bed arrangement--physically mixed bed and separated bed--were considered and compared by computer simulation. The simulations reveal that adding MgO in the separated bed by packing MgO before WO_3/SiO_2 offers superior propylene yield to the physically mixed bed. The appropriate %MgO loading in catalyst bed which offers a maximum propylene yield was found to vary (3 and 23%), depending on operating condition.

Keywords: Metathesis, Propylene, 1-Butene Isomerization, Kinetics, Catalyst Bed Design

INTRODUCTION

There are many ways to produce propylene, such as propane dehydrogenation [1], naphtha thermal crackers [2], Fischer-Tropsch synthesis [3] and metathesis reaction. The process of propylene production by metathesis was discovered by Philips Petroleum Company. However, in recent years, this process has gained a significant attention from researchers due to an increase in propylene global demand [4-8]. Substantial thoughts have been given to improving the metathesis process. For instance, a method of changing the catalyst was done jointly between the Institut Français du Pétrole (IFP) and the Chinese Petroleum Corporation (Kaoshiang, Taiwan). In their process, ethylene and 2-butene react in liquid phase in the presence of Re_2O_7/Al_2O_3 catalyst at 308 K and 60 bar. Although, the operating condition is more favorable under this method, the cost of catalyst and high purity of feed requirement prevents this method from becoming commercialized [9,10]. There have also been several attempts to improve the propylene yield by changing the reactor type. For example, distillation column reactor and fluidized bed reactor have been successfully attempted [11,12].

In addition to the above approach, some researchers are focusing on feed alternatives. For example, ethylene and 2-pentene can react to produce propylene and 1-butene [13]. Another interesting approach is based on non-ethylene feed. We focus here on this approach. The reason is that there has been a significant increase in demand on ethylene. In China alone, the annual production of ethylene rapidly increased from 9.9 megatons to 16.2 megatons between 2008 and 2013 [14]. By alternative process, propylene can be made by feeding 1-butene and 2-butene. Normally, it is impossible to produce propylene if 1-butene is the only reactant used [15]. However with the presence of bi-functional catalysts, it is possible to produce propylene by using only 1-butene as reactant feed. Bi-functional catalysts engage in both isomerization activity as well as metathesis activity. During isomerization, some 1-butene is converted into 2-butene. Then, during metathesis, both 1-butene and 2-butene react to form propylene and byproducts. Examples of such catalysts are MoO_3 and WO_3 [16].

With bi-functional catalysts, the rate of propylene production is affected by both the rate of isomerization as well as the rate of metathesis. Therefore, it is beneficial to be able to determine whether or not the amount of isomerization activity is already sufficient for an optimal production of propylene. There is also a question of whether it would be desirable to increase the amount of isomerization activity by adding an isomerization catalyst. Magnesium oxide, zinc oxide and zirconium oxide are the most common isomerization catalysts [17-19].

This work focuses on designing beds of heterogeneous catalysts for conversion of 1-butene to propylene. The selected bi-functional catalyst WO_3/SiO_2 is a well-known metathesis catalyst for the conventional ethylene and 2-butene feed because it is very resilient to frequent poisoning and shows good activity and selectivity for a long period of time [20]. For isomerization catalyst, MgO is selected due to its reputation as being an effective catalyst for isomerization [19]. It is also among the most common catalysts used in the conventional feed process [21,22]. The focus of this work was to propose the improvement of propylene production by addition of MgO isomerization catalyst. Moreover, a suitable catalyst bed arrangement of WO_3/SiO_2 and MgO was explored. The study was conducted by determining reaction rate expressions over the two catalysts modelling and simulating the reaction system to find the optimum

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catalyst ratio and bed arrangement.

EXPERIMENTAL

To evaluate the kinetic constants of all metathesis reactions in 1-butene metathesis, the powders of MgO and WO_3/SiO_2 were used (particle size lower than 250 µm). This was to avoid all internal mass transfer effect [23]. Furthermore, by considering the Weisz-Prater criterion using the experimental data, it was demonstrated that the internal mass transfer effect is insignificant for this work. In addition, by following the Mears criterion [24,25], it was proved that the external mass transfer effect is also negligible in the range of operating conditions selected in this study.

The catalyst was packed in a fixed bed reactor (0.75 inch inner diameter) held by plugs of quartz wool on both ends starting from 0.5 cm over thermocouple to the center of the reactor, then the experiment was carried out. The catalyst weight was 1 g for MgO and it was 3 g for WO_3/SiO_2. After the catalyst was pretreated at 773 K under 0.1 MPa by N_2 (99.9% purity 30 ml/min) for 1 h, it was cooled to the reaction temperature. The gaseous feed of 10% 1-butene balanced N_2 was fed downward through the packed catalyst and the effluent stream was analyzed by a gas chromatograph with an FID detector. The reactions were under atmospheric pressure and a reaction temperature of between 623 and 723 K. For MgO, volumetric flow rate was studied in the range of 10-40 ml/min and reaction time was 10 hours. For WO_3/SiO_2, volumetric flow rate was studied in the range of 10-55 ml/min and reaction time was 30 hours. Catalytic performance was investigated. All instruments were set up as shown in Fig. 1. All the experiments were carried out at atmospheric pressure. After reaching steady state, the catalytic activities were very stable with no deactivation detected. Some experiments were tested for as long as 72 hours without observing deactivation. A catalyst sample after reaction was tested using temperature programmed oxidation (TPO) technique, it was found that the amount of carbon was less than 0.07 wt%, indicating that the coke formation was small.

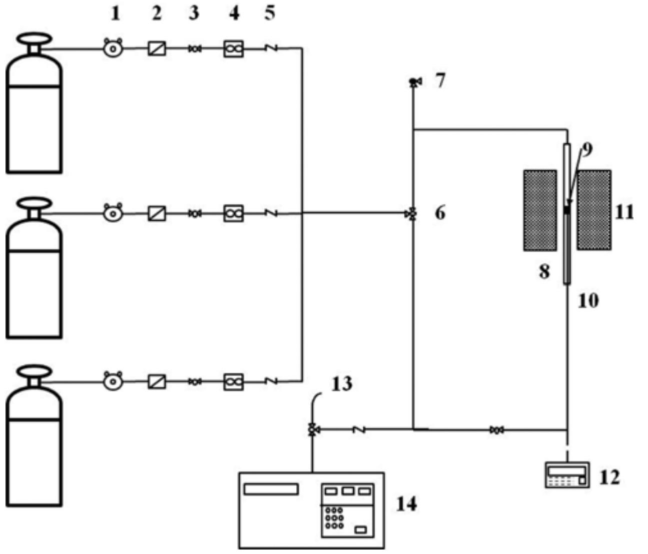

Fig. 1. Schematic of reaction system.

1. Pressure regulator
2. Filter
3. On-off valve
4. Mass flow controller
5. Check valve
6. 3-Ways
7. Relief valve
8. Reactor
9. Catalyst bed
10. Thermocouple
11. Electric furnace
12. Heater control
13. Open vent
14. Gas chromatograph

MODELING

In this work, the overall reaction pathways occur as shown in Eqs. (1) to (5).

$$\text{1-butene} \overset{k_1}{\underset{k_{-1}}{\Leftrightarrow}} \text{2-butene} \tag{1}$$

$$\text{1-butene+2-butene} \overset{k_2}{\underset{k_{-2}}{\Leftrightarrow}} \text{propylene+2-pentene} \tag{2}$$

$$\text{1-butene+1-butene} \overset{k_3}{\underset{k_{-3}}{\Leftrightarrow}} \text{ethylene+3-hexene} \tag{3}$$

$$\text{ethylene+2-butene} \overset{k_4}{\underset{k_{-4}}{\Leftrightarrow}} \text{2 propylene} \tag{4}$$

$$\text{ethylene+2-pentene} \overset{k_5}{\underset{k_{-5}}{\Leftrightarrow}} \text{1-butene+propylene} \tag{5}$$

MgO catatyst was found to be active for the isomerization (Eq. (1)). However, WO_3/SiO_2 catalyst is active for all the reactions (Eqs. (1) to (5)). By following the previous work on metathesis [26], the reactions were assumed to be elementary reactions and no isomerization among different 2-butenes (cis and trans) was considered. In addition, although iso-butene is also a possible reaction product, the experimental results showed that iso-butene was found to be lower than 0.5% at 723 K and was not detected at 623 K. Therefore, in this study, the iso-butene was also neglected in the equations. The isomerization reaction is first order and the metathesis reactions are second order. Note that the rates of reaction in Eq. (1) to Eq. (5) can be given as Eqs. (6) to (10), respectively, where A=1-butene, B=2-butene, C=propylene, D=2-pentene, E=ethylene, F=3-hexene

$$R_1=k_1C_A-k_{-1}C_B \tag{6}$$

$$R_2=k_2C_AC_B-k_{-2}C_CC_D \tag{7}$$

$$R_3=k_3C_AC_A-k_{-3}C_EC_F \tag{8}$$

$$R_4=k_4C_BC_E-k_{-4}C_CC_C \tag{9}$$

$$R_5=k_5C_DC_E-k_{-5}C_AC_C \tag{10}$$

The rate constants of reversible paths were calculated by using the relationship between rate constant and equilibrium rate constant (Eq. (11)). For heterogeneous system, the designed equation for a packed-bed catalytic reactor can be written as Eq. (12) where F_i is molar flow rate of i species gas and W is weight of the catalyst and r'_i is rate of reaction of species i. It is reasonable to write the rate expression of MgO catalyst reaction in the form of Eqs. (13) to (14) and WO_3/SiO_2 catalyst reaction in form of Eqs. (15) to (20).

$$K_{eq}=\frac{k_1}{k_{-1}} \tag{11}$$

$$\frac{dF_i}{dW} = r'_i \quad (12)$$

$$r'_A = -R_1 \quad (13)$$

$$r'_B = R_1 \quad (14)$$

$$r'_A = -R_1 - R_2 - 2R_3 + R_5 \quad (15)$$

$$r'_B = R_1 - R_2 - R_4 \quad (16)$$

$$r'_C = R_2 + 2R_4 + R_5 \quad (17)$$

$$r'_D = R_2 - R_5 \quad (18)$$

$$r'_E = R_3 - R_4 - R_5 \quad (19)$$

$$r'_F = R_3 \quad (20)$$

To solve multiple ordinary differential Eqs. (6) to (20), to obtain all reaction rate constants, k_i, 4th Runge-Kutta method was selected. Under this method, the experimental data was laid out and compared to the results from the simulation. Then, the least square fitting method was used to determine A_0 and E_a in Arrhenius Equation in Eq. (21), which would yield kinetic rate constants. These kinetic rate constants were further used in the model simulation.

$$k_i = A_0 e^{\frac{E_a}{RT}} \quad (21)$$

A catalyst bed offering the highest propylene was optimized using computer simulation. Two types of catalyst bed arrangement shown in Fig. 2 were considered. The first type is separated bed (MgO first and WO_3/SiO_2 followed) and the second type is physically mixed bed. The total catalyst is fixed at 3 g for both cases.

RESULTS AND DISCUSSION

To find the rate constant of MgO, experiments at three temperatures of 623, 673, 723 K and various feed flow rates were performed. The exit molar flow rates of different gases were used to determine best-fitted kinetic parameters. In Fig. 3, symbols represent experimental data, while lines represent results from simulations. When increasing the temperature, the molar flow rate of 1-butene decreases, while the molar flow rate of 2-butene increases. This can be interpreted as that the rate constant of 1-butene to 2-

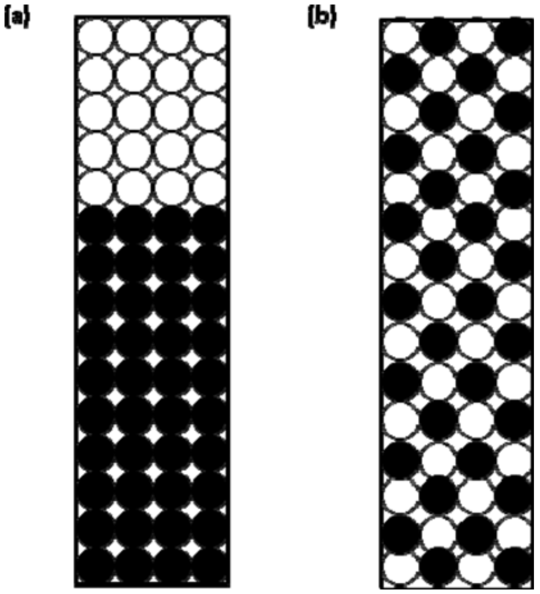

Fig. 2. Types of catalyst bed: (a) Separated bed, (b) physically mixed bed.

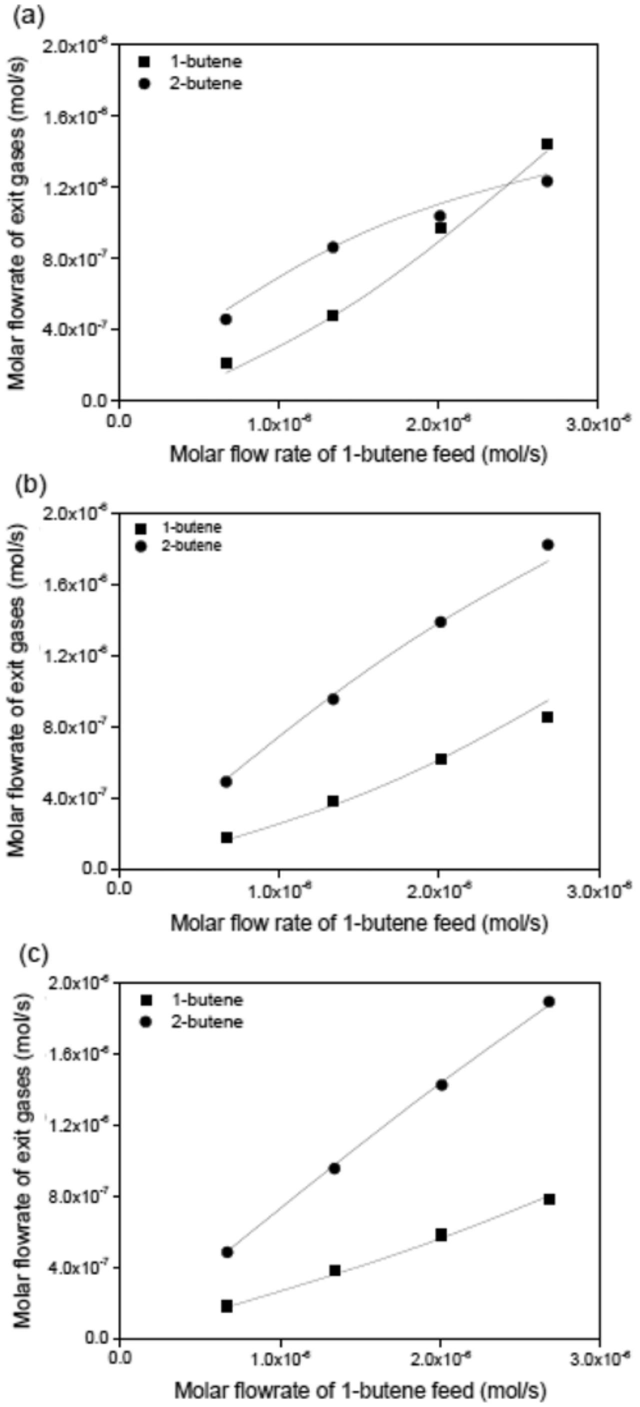

Fig. 3. Molar flow rates of different gas products from 1-butene isomerization at different temperatures: (a) T=623 K, (b) T=673 K, (c) T=723 K (catalyst=1 g of MgO, 1-butene feed=6.70×10^{-7}, 1.34×10^{-6}, 2.01×10^{-6} and 2.68×10^{-6} mol/s, symbols represent experimental data, Lines represent simulation data).

Table 1. Estimated values of the kinetic parameters on MgO isomerization catalyst and WO_3/SiO_2 metathesis catalyst

Rate constants	A_0	E_a (kJ/mol)	R^2*
k_{1MgO}	1.08×10^1 $m^3/(kg\cdot s)$	4.78×10^1	0.9953
k_{-1MgO}	2.03×10^1 $m^3/(kg\cdot s)$	5.78×10^1	0.9969
k_1	2.83×10^{-3} $m^3/(kg\cdot s)$	8.49×10^0	0.9999
k_{-1}	5.33×10^{-3} $m^3/(kg\cdot s)$	1.84×10^1	0.9999
k_2	1.88×10^5 $m^6/(mol\cdot kg\cdot s)$	7.66×10^1	0.9993
k_{-2}	1.22×10^5 $m^6/(mol\cdot kg\cdot s)$	7.64×10^1	0.9993
k_3	1.71×10^5 $m^6/(mol\cdot kg\cdot s)$	8.65×10^1	0.9916
k_{-3}	8.26×10^5 $m^6/(mol\cdot kg\cdot s)$	8.48×10^1	0.9915
k_4	2.19×10^{11} $m^6/(mol\cdot kg\cdot s)$	1.59×10^2	0.9983
k_{-4}	6.50×10^{10} $m^6/(mol\cdot kg\cdot s)$	1.62×10^2	0.9984
k_5	7.31×10^{11} $m^6/(mol\cdot kg\cdot s)$	1.85×10^2	0.9978
k_{-5}	3.18×10^{11} $m^6/(mol\cdot kg\cdot s)$	1.87×10^2	0.9979

*Coefficient of determination

butene isomerization increases as the temperature becomes higher. Note that no other products were detected from the isomerization reaction of 1-butene over MgO. The rate constants of MgO are displayed in Table 1 as k_{1MgO} and k_{-1MgO}.

To find the rate constants of WO_3/SiO_2 bi-functional catalyst, similar experiments were performed. From Fig. 4, when increasing the temperature, the molar flow rates of propylene, 2-pentene, ethylene and 3-hexene increase. However, the molar flow rates of 1-butene and 2-butene drop. Note that the molar flow rate of propylene is higher than that of 2-pentene. This also applies to 3-hexene, which is higher than ethylene. This is valid for all the temperature ranges in the experiments, particularly at the highest temperature (723 K). This can be explained by the fact that 1-butene can undergo self-metathesis, producing ethylene and 3-hexene as shown in Eq. (3). The ethylene produced by Eq. (3) can be a reactant for Eqs. (4) and (5) via cross-metathesis, which results in more propylene in the system [16,27]. The rate constants of all reactions in metathesis reaction are also summarized in Table 1.

Referring to the rate constants in Table 1, it is obvious that the isomerization activity of MgO far exceeds that of WO_3/SiO_2. The gaps become even more significant at higher temperatures. It is twice at 623 K and grows to about 5 times at 723 K. From the rate constant obtained, it is interesting that at low temperature, an alternative process (Eq. (2)) plays an important role. However, as the temperature rises, the conventional process rate (Eq. (4)) becomes more pronounced compared to the alternative process rate and eventually exceeds the alternative process rate.

After the rate constants are obtained, they are used in simulations. The goal of the simulation is to find the best method to combine MgO and WO_3/SiO_2 that would maximize the molar flow rate of the propylene. The weight of catalyst is fixed at 3 g for every test. Two catalyst bed arrangements are considered.

The first case is a physically mixed bed. The simulation results on the exit molar flow rate and yield of propylene when using different ratios of MgO to WO_3/SiO_2 and temperature for three values of 1-butene molar flow rate (2.68×10^{-6}, 3.69×10^{-6}, 7.37×10^{-6} mol/s) are shown in Fig. 5. The %weight of MgO of 0 represents the catalyst bed of only WO_3/SiO_2 catalyst. It is found that when the temperature increased, propylene yield also increased. However, when the molar flow rate of 1-butene feed increased, the yield dropped. For example, at 723 K and molar flow rate of 1-butene feed is 2.68×10^{-6} mol/s, the propylene yield was in a range between 13% and 18%. On the other hand, it dropped to 6% to 8% at molar flow rate of 7.37×10^{-6} mol/s. It was found that when MgO is intro-

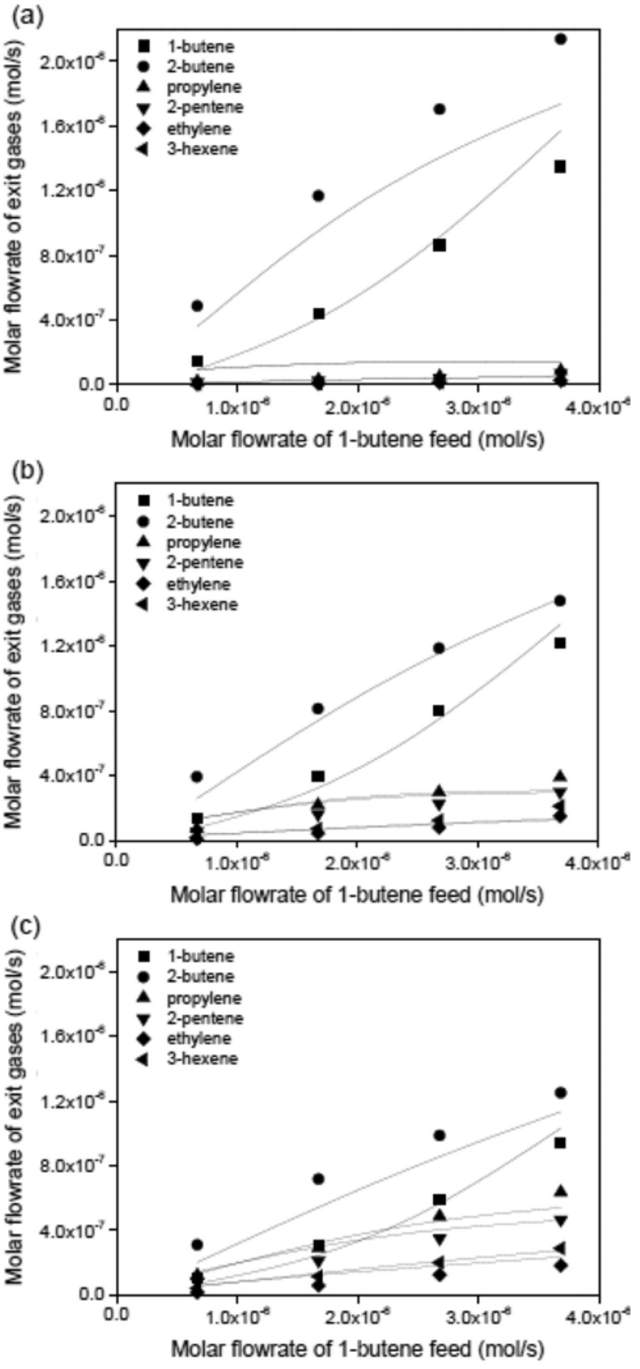

Fig. 4. Molar flow rates of different gas products from 1-butene metathesis at different temperatures: (a) T=623 K, (b) T=673 K, (c) T=723 K (catalyst=3 g of WO_3/SiO_2, 1-butene feed=6.7×10^{-7}, 1.68×10^{-6}, 2.68×10^{-6} and 3.69×10^{-6} mol/s, symbols represent experimental data, Lines represent simulation data).

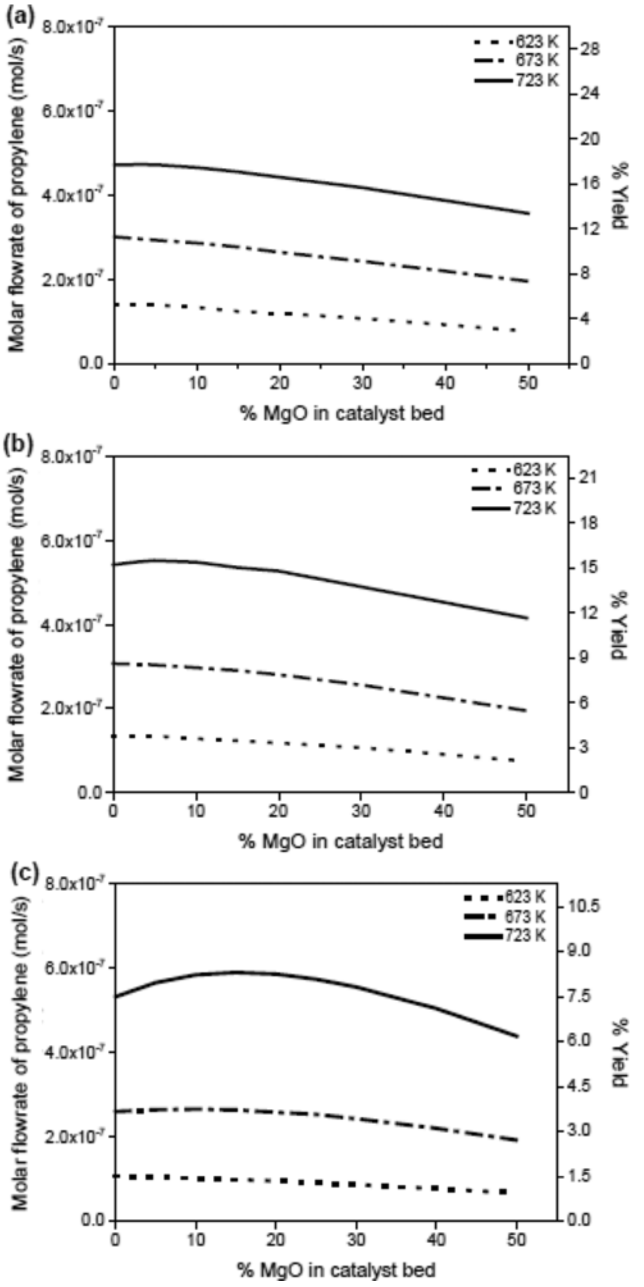

Fig. 5. Effect of % MgO in catalyst bed and temperature on outlet molar flow rate of propylene and propylene yield at different molar flow rate feed of 1-butene: (a) 2.68×10^{-6} mol/s, (b) 3.69×10^{-6} mol/s, (c) 7.37×10^{-6} mol/s (physically mixed bed, total catalyst weight=3 g).

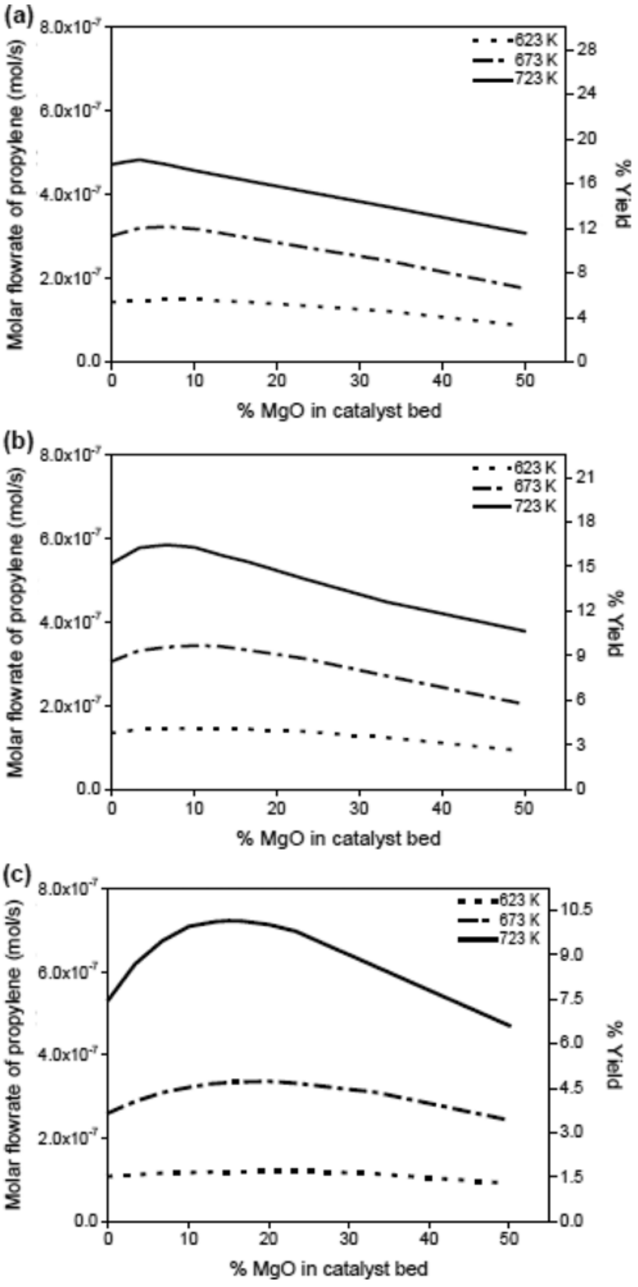

Fig. 6. Effect of % MgO in catalyst bed and temperature on outlet molar flow rate of propylene and propylene yield at different molar flow rate feed of 1-butene: (a) 2.68×10^{-6} mol/s, (b) 3.69×10^{-6} mol/s, (c) 7.37×10^{-6} mol/s (separated bed, total catalyst weight=3 g).

duced into the bed, the propylene output decreases as MgO gets proportionately bigger under physically mixing arrangement. However, at higher molar flow rate and temperature, adding an appropriate amount of MgO increased the propylene yield. For instance, the yield increased from 7% to 8% at flow rate of 7.37×10^{-6} mol/s and 723 K when MgO is increased to 15% of the total catalyst bed.

The second arrangement, the separated bed, was simulated under the same condition as the previous physically mixed bed arrangement. The results are shown in Fig. 6. It is obvious that the results resembled those of the physically mixed bed arrangement, that is, the propylene yield increased when the temperature increased. Furthermore, when the molar flow rate of 1-butene feed increased, the yield dropped. The main difference of the results for the separated bed arrangement compared to the physically mixed arrangement is that for every condition of separated bed arrangement, adding more MgO into the catalyst bed would yield more propylene yield until it reached the optimal point, then the yield dropped.

Table 2. %Improvement of propylene production rate at optimum MgO loading compared with pure WO_3/SiO_2 at different temperature and different molar flow rate of 1-butene feed

T (K)	Molar flow rate of 1-butene feed (mol/s)	%Improvement of separated bed	%Improvement of physically mixed bed
623	2.68×10^{-6}	4	0
	3.69×10^{-6}	8	0
	7.37×10^{-6}	11	0
673	2.68×10^{-6}	7	0
	3.69×10^{-6}	12	0
	7.37×10^{-6}	29	2
723	2.68×10^{-6}	2	0
	3.69×10^{-6}	8	2
	7.37×10^{-6}	36	11

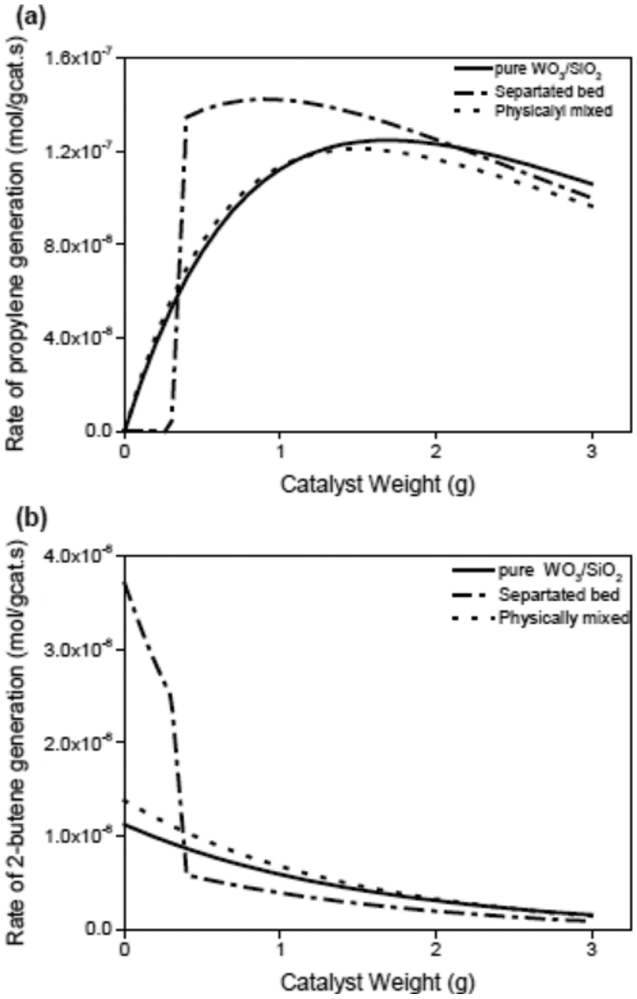

Fig. 7. Profiles of product generation rates for different bed arrangement on 10% MgO in total catalyst of 3 g and temperature of 673 K: (a) rate of propylene generation, (b) rate of 2-butene generation.

For the conditions which offer maximum amount of propylene, the amount of MgO needed is less when the temperature is higher. As can be seen on the graph, at 2.68×10^{-6} mol/s initial feed, the required amount of MgO is 10%, 7% and 3% at 623, 673 and 723 K, respectively. The optimal amount of MgO needed directly correlates to the increasing molar flow rate of 1-Butene feed. This can be clearly seen on the graph. At 3.69×10^{-6} mol/s initial feed, the required amount of MgO is 12%, 10%, 7% at 623, 673 and 723 K, respectively. The required amount is even higher at 7.37×10^{-6} mol/s initial feed (23%, 20% and 15% at 623, 673 and 723 K respectively). Note that the higher the molar feed flow rate, the larger the difference in propylene output rate between having an optimal amount of MgO in the catalyst bed, and not having any MgO at all. Table 2 shows the difference in percentage term. Therefore, if there is an appropriate amount of MgO in the catalyst bed, it can be seen that packing catalyst under separated bed arrangement would yield higher propylene produced than the mixed bed arrangement.

To compare the results between the two arrangements, separated bed and physically mixed bed, the rates of propylene and 2-butene generation were investigated at 10% MgO in total catalyst 3 g and temperature of 673 K, which is the point where propylene is maximum under the separated bed arrangement for the initial 1-butene flow rate of 3.69×10^{-6} mol/s as shown in Fig. 7. From the rate of propylene generation, the separated bed arrangement initially produces much higher rate than using the only WO_3/SiO_2 and the physically mixed arrangement because the separated bed arrangement can produce 2-butene, which is a reactant, faster than the other methods. However, eventually at the end of the catalyst bed, the rate for separated bed arrangement falls behind the only WO_3/SiO_2 case. This is because the separated bed arrangement produces propylene noticeably faster than the other two methods. So, it reaches equilibrium quicker. For the physically mixed arrangement, the rate of propylene generation is slightly higher than the pure WO_3/SiO_2 case because of the MgO mixed in the catalyst bed. The MgO in the physically mixed arrangement allows the reactant (2-butene) to form faster and, thus, the propylene generates at a faster rate. However, at the end, the rate of propylene generation by physically mixed arrangement falls behind the rate of using only WO_3/SiO_2 case. This is explained by the fact that some MgO in the mixed bed occupies some of the space of metathesis catalyst. When reactants are ready (meaning there is no need for isomerization anymore, the ratio of 1-butene to 2-butene is appropriate), the decrease in the metathesis catalyst results in decrease in propylene production.

To explain that some MgO in the mixed bed occupies some of the space of metathesis catalyst, it can be seen from the 2-butene generation graph that packing the catalyst by the physically mixing arrangement results in higher rate of 2-butene generation than using only WO_3/SiO_2 and separated bed arrangement. This produced 2-butene instead of propylene, and is the reason why the arrangement of physically mixing the catalyst is not the best arrangement for practical usage.

CONCLUSION

The rate constants of isomerization and metathesis reactions on MgO isomerization catalyst and WO_3/SiO_2 bi-functional catalyst were determined and used to simulate the propylene production from 1-butene alternative feed. Considering two types of catalyst bed arrangement, it was found that there is an optimal %MgO loading that offers a maximum propylene yield for each operating condition, and the separated bed of MgO and WO_3/SiO_2 is more favorable than the physically mixed bed. This is because the former can efficiently utilize the metathesis activity of the WO_3/SiO_2.

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NOMENCLATURE

A_0 : pre-exponential factor
C_i : concentration of species i [mol/dm^3]
E_a : apparent activation energy [kJ/mol]
F_i : molar flow rate of species i in the fixed bed reactor [mol/s]
k_i : apparent rate constant for the i^{th} reaction
K_{eq} : equilibrium rate constant
R : gas constant [J/mol·K]
R_i : rate of reaction in equation i [mol/kg·s]
r'_i : rate of reaction in species i [mol/kg·s]
T : temperature [K]
W : catalyst weight [kg]

Symbols

A : 1-butene
B : 2-butene
C : propylene
D : 2-pentene
E : ethylene
F : 3-hexene

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