Room-temperature isomerization of 1-butene to 2-butene over palladium-loaded silica nanospheres catalyst

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HIGHLIGHTS

- Study of the 1-butene isomerization at room temperature over supported Pd catalyst.
- The surface acidity of catalyst had remarkably influences on catalytic activity.
- Oxygen greatly enhanced the conversion without the formation of carbon dioxide.
- The butenylcarbenium ion intermediate determined the *trans:cis* ratio of 2-butene.

GRAPHICAL ABSTRACT

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ABSTRACT

The traditional reaction temperatures of 1-butene isomerization to 2-butene tend to above 100 °C, while here we report the unique catalytic performance of a Pd loaded silica nanospheres catalyst for 1-butene double-bond-shift isomerization at room temperature and showed 2-butene yield of 37.0%. Furthermore, the introduction of O₂ into the reaction mixture dramatically improved the yield efficiency to 57.2% without the formation of by-product CO₂. The reaction process is proved that the ratio of *trans*-2-butene to *cis*-2-butene in the final product was determined by the *trans:cis* ratio of the butenylcarbenium ion intermediate, and the ratio of *trans*-2-butene to *cis*-2-butene decreased with the increasing reaction temperature. Unlike other palladium catalyst systems, Pd⁰ nanoparticles were proved to act as catalytic active sites, and their oxidation and aggregation resulted in a decrease in activity. Most importantly, the catalyst acidity affected the catalytic performance, which provides theoretical basis for the choice of catalysts.

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1. Introduction

Various chemical processes produce C₄ cuts containing a substantial proportion of 1-butene. However, for some kinds of use, it is preferred to obtain a high content of 2-butene. For example,

in the HF-alkylation process of crude oil refining industry, 2-butene is a better feedstock than 1-butene because 2-butene would lead a much lower amount of the less valuable dimethylhexanes [1,2]. What's more, as one of the major raw materials used in industrial organic chemistry, propene could also be obtained by the metathesis of 2-butene and ethene [3,4]. The isomerization of 1-butene to 2-butene is a green catalytic process and has become more attractive in terms of lower overall costs.

Due to the limited applications of 2-butene in past industrial processes, studies on butene have focused primarily on the skeletal

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isomerization of 1-butene to iso-butene [5–8] and the *trans*–*cis* isomerization of 2-butene [9–12]. Some earlier studies [13] focused on the thermodynamic data and reaction mechanism of 1-butene isomerization reaction. Although 2-butene is a thermodynamically stable isomer, a relatively high reaction temperature is needed to overcome the activation barrier for the isomerization of 1-butene. The thermodynamic equilibrium is unfavorable to the conversion of 1-butene to 2-butene at high temperature. Besides, the higher reaction temperature, the greater energy consumption and which will also produce extra exhaust emissions. The by-products of isomerization reaction such as CO₂ are also easy to generate, therefore studies about introducing oxygen (O₂) into the reaction mixture have been rare. Running the isomerization reaction at room temperature allows the effects of O₂ to be evaluated.

Perissinotto et al. [14] prepared a series of acid-leached meta-kaolin and tested the catalytic performance of 1-butene double-bond-shift isomerization. The highest conversion was about 90.0% with a selectivity of 71.7%, even under the harsh reaction conditions ($T = 400\text{ }^{\circ}\text{C}$). Puriwat et al. [15] investigated the isomerization of 1-butene over a MgO/Mg(OH)₂ catalyst at 300 °C, obtaining a conversion of only 20–70%. Li et al. [16] synthesized Cs/zeolite X catalysts and conducted the same reaction at 100 °C, attaining a relatively high conversion of 1-butene (81%). This reaction has also been examined in ionic liquids (e.g., EmimF [17] and EmimCl [18]) using computational methods. However, several challenges remain in performing the analogous experimental studies, and the use of ionic liquids severely restricts practical applications. Amigues et al. [19] developed supported noble metal (from group VIII of the periodic classification of elements) catalysts for isomerizing 1-butene to 2-butene from 50 °C to 140 °C, while the catalyst should be pretreated using sulfur compound and subsequently hydrogen.

As a kind of those noble metals, palladium (Pd) has been used as a catalytically active phase in various organic synthesis, including cross-coupling reactions [20,21] and hydrogenation reactions [22], and has shown excellent catalytic activity and selectivity. Palladium had also been proved to be active for 1-butene isomerization reaction at lower temperature. Sen et al. [23] used two different substrates, [Pd(CH₃C–N)₄(BF₄)₂] and its tertiary phosphine derivatives as catalyst and CH₃CN or CHCl₃ were used as solvents. They found Pd²⁺ was the active site for 1-butene double-bond-shift isomerization reaction. Note that unlike the technique commonly used in industry, their work was conducted under homogeneous conditions, combined with the high costs of complex catalysts, determining that this reaction system will be difficult to be practically applied. Carrá et al. [24] employed supported Pd catalyst for 1-butene isomerization reaction from 160 °C to 240 °C and proved two different mechanisms, one of which showed a stereoselectivity towards *cis*-2-butene. Recently, Kominami et al. [25] developed a series of highly active Pd/TiO₂ catalysts prepared by a photodeposition method and conducted a 1-butene double-bond-shift isomerization reaction under UV irradiation. Unfortunately, no isomerization occurred in the dark (even at 70 °C) or under visible light.

The aforementioned studies seem to indicate that some amount of energy must be supplied (heat or light) to facilitate the isomerization of 1-butene to 2-butene. The current study describes the use of a supported Pd catalyst for the room-temperature isomerization of 1-butene without the addition of extra energy. Unlike the previous reports, we found Pd⁰ nanoparticles were also efficient for the titled reaction at room temperature. Furthermore, this study explores the influences of surface acidity and O₂ on the double-bond-shift isomerization reaction.

2. Experimental section

2.1. Chemicals and materials

Palladium chloride (PdCl₂, Sinopharm Chemical Reagent Co., Ltd., AR), chloroauric acid (HAuCl₄·4H₂O, Sinopharm Chemical Reagent Co., Ltd., AR), and chloroplatinic acid (H₂PtCl₆·6H₂O, Sinopharm Chemical Reagent Co., Ltd., AR) were used as noble metal precursors.

Silica nanospheres (SNS, Aladdin Reagent Co., Ltd., 99.5%), Silicon dioxide (SiO₂, Degussa Co., Ltd., 99.8%), H-BEA zeolite (Nankai University Catalyst Co., Ltd.), ZSM-5 zeolite (Nankai University Catalyst Co., Ltd.), aluminum sesquioxide (Al₂O₃, Shandong Aluminum Co., Ltd.), and titanium dioxide nanopowder (TiO₂, Aladdin Reagent Co., Ltd., 99.5%) were selected as supports.

Sulfuric acid (H₂SO₄, Sinopharm Chemical Reagent Co., Ltd., GR) was used to treat with catalysts.

The reaction feed consisted of 5% butene (99.3%) and various amounts of O₂ in N₂.

2.2. Synthesis of catalysts

Noble metal-loaded catalysts were prepared using an impregnation (IMP) [26] method. The total noble metal loading of prepared catalysts was kept at 1.0 wt.%. In a typical procedure, 2 g of the support was impregnated with an aqueous solution of a noble metal precursor at the desired mass ratio and kept overnight. After drying at 100 °C, the samples were soaked in 2% aqueous ammonia and washed with ultrapure water (18 MΩ resistivity). After drying at 100 °C overnight, the catalysts were reduced in H₂ at 300 °C for 3 h, and then exposed in N₂ to remove residual H₂.

Pd/SNS and Pd/SiO₂ catalysts were also leached with acid aqueous solution for further study. The catalysts were soak in 1M H₂SO₄ aqueous solution for 20 min, and then filtered to remove the residual solution. The catalysts were finally dried at 60 °C for 2 h and labeled as catalyst-H₂SO₄.

All of the catalysts were crushed and sieved using 40 mesh prior to use.

2.3. Catalytic activity measurements for butene isomerization

Catalytic tests were performed using a fixed glass U-tube reactor (6 mm inner diameter) loaded with 0.20 g of catalyst. The U-tube was wrapped with aluminum foil to simulate dark conditions and immersed in a water bath. The reaction feed flow rate was maintained at 20 mL min^{−1} [weight hourly space velocity (WHSV) of 6000 mL g^{−1} h^{−1}]. The reactants and products were analyzed using an Agilent 7890A gas chromatograph equipped with a flame ionization detector (HP-PLOT Al₂O₃ S column) and a thermal conductivity detector (TDX-01 column).

The catalyst behavior was evaluated in terms of the following parameters, where F is the molar flow rate and subscripts i and o indicate values measured at the inlet and outlet, respectively:

$$\text{Conversion}^{1\text{-butene}} = \frac{F_i^{1\text{-butene}} - F_o^{1\text{-butene}}}{F_i^{1\text{-butene}}} \times 100\%$$

$$\text{Yield}^{2\text{-butene}} = \frac{F_o^{2\text{-butene}}}{F_i^{1\text{-butene}}} \times 100\%$$

$$\text{Ratio}^{\text{trans-cis}} = \frac{\text{Yield}^{\text{trans-2-butene}}}{\text{Yield}^{\text{cis-2-butene}}}$$

2.4. Materials characterization

The Zeta potential was measured on a Malvern Zetasizer 2000. The samples were dispersed in water and tested for three times.

NH_3 temperature-programmed desorption (NH_3 -TPD) experiments were conducted carried out on a Micromeritics Chemisorb 2720 apparatus in a range of room temperature to 600 °C ($10^\circ\text{C min}^{-1}$). About 80 mg samples were heated at 100 °C in pure He for 3 h, and 2.0% NH_3/He was fed to the reactor for 30 min at room temperature. Then pure He was fed to the reactor at 50 mL min^{-1} for 30 min to purge away any residual NH_3 . The samples were then tested in a pure He flow.

X-ray photoelectron spectra (XPS) were recorded with a Thermo ESCALAB 250 instrument using $\text{Al } K_\alpha$ radiation. The base pressure was 5×10^{-8} Pa. Binding energies were calibrated using the C (1s) peak of contaminant carbon ($\text{BE} = 285$ eV) as the standard and quoted with a precision of ± 0.2 eV.

H_2 temperature-programmed reduction (H_2 -TPR) experiments were also studied on the Micromeritics Chemisorb 2720 apparatus in a range of room temperature to 250 °C ($10^\circ\text{C min}^{-1}$). About 80 mg samples were preheated at 120 °C for 30 min and tested in a H_2/He flow (5%, 50 mL min^{-1}).

Field-emission scanning electron microscopy (FE-SEM) images were obtained on Hitachi SU 8020 equipment, with a tungsten electron source and an accelerating voltage from 1.0 kV.

High-resolution transmission electron microscopy (HR-TEM) micrographs were obtained with a JEOL 2011 instrument at an acceleration voltage of 200 kV. The specimens were prepared by ultrasonic dispersion in ethanol and evaporating a drop of the resultant suspension onto ultrathin carbon supporting films.

3. Results and discussion

3.1. Catalytic performance of noble metal-supported catalysts

As shown in Fig. 1, the Pd/SNS catalyst exhibited an excellent catalytic activity with a 47.6% yield of 2-butene without the formation of by-products such as CO_2 . Gold (Au) and platinum (Pt) were inactive under the same reaction condition. When Pd was partially replaced by Au at a Au:Pd mass ratio of 1:1, the decline in Pd loading resulted in a yield of only 21.8%. It's worth noting that, the unreduced Pd/SNS catalyst was inactive at the same reaction condition, which is the difference from the reported $\text{Pd}^{+\delta}$ catalyst systems [23].

Fig. 1. Catalytic activities over various noble metal supported on SNS catalysts. The molar ratio of O_2 :1-butene was 1:1 and the reaction temperature was 25 °C. The Pd/SNS* catalyst was not reduced by H_2 .

Other silica materials may be also efficient supports for this reaction (shown in Fig. 2). KIT-6 is a molecular sieve composed of pure silica [27], and the yield of 1-butene over Pd/KIT-6 was 21.2%. A Pd/H-BEA catalyst exhibited a similar yield of 31.1%. While Pd supported on other supports, even another kind of commercial silica material, exhibited nearly negligible activities for this reaction.

3.2. Effect of the surface acidity on catalytic performance

For supported Pd catalyst, there is a strong synergistic interaction between noble metal nanoparticles and support, which can greatly enhance the catalytic activity and selectivity [28,29], and the different catalytic activities resulted from supports, which could be partly explained by their corresponding Zeta potentials of those catalysts (shown in Fig. 2a). The Zeta potentials of active catalysts were below -20 mV, suggesting the surface of those catalysts was acidic. According to Kominami's study, the UV irradiation is essential for 1-butene isomerization over Pd/ TiO_2 under room temperature because it is a controllable substitute for the acidity of catalyst [25].

Total acidity measurements of catalysts were observed by NH_3 temperature-programmed desorption and were shown in Fig. 2b. The catalysts exhibiting activities in 1-butene double-bond-shift isomerization reaction had an evident desorption peak of ammonia around 100 °C. The peak can be assigned to NH_3 adsorption on the

Fig. 2. Effect of the surface acidity on catalytic performance. (a) Correlation between catalytic activities and Zeta potential, and (b) NH_3 -TPD profiles of supported Pd catalysts.

weak acid sites [30,31]. The peak area broadly increased with the yield of 2-butene enhanced, suggesting the surface weak acid sites have positive impacts on the catalytic performances as reported [32–34].

To further examine that the surface acidity of Pd-loaded catalysts has important effects on the catalytic activities, 1M H_2SO_4 aqueous solution was used to leach the two kinds of catalysts carried in silica (Pd/SNS and Pd/SiO_2) and tested in the titled reaction at room temperature. As shown in Fig. S3, after the treatment, the yield of 2-butene over Pd/SiO_2 catalyst which was originally inactive increased to 43.9% and 1-butene almost completely convert to 2-butene over $\text{Pd}/\text{SNS}-\text{H}_2\text{SO}_4$ catalyst. This acid-leached method is effective for 1-butene double-bond-shift isomerization reaction and would be further studied.

3.3. Influences of the reaction conditions

The effects of reaction temperature and the presence of O_2 on the catalytic activity of Pd/SNS catalysts were evaluated, and the results are shown in Fig. 3a. The double-bond-shift isomerization of 1-butene was initiated at temperatures as low as 0°C . The only detected product was 2-butene and its *trans*:*cis* ratios were between 1.5 and 2.7, which decreased with increasing reaction temperature. Initially, the yield of 2-butene was about 37.0% at 25°C . To the best of our knowledge, this is the highest yield efficiency reported at room temperature without light irradiation so far.

Fig. 3. Influences of the reaction conditions. (a) Catalytic activities over Pd/SNS catalyst at different reaction conditions at an O_2 :1-butene ratio of 1:1, and (b) catalytic activities over Pd/SNS catalyst at 25°C .

In the prior research, the effect of molecular O_2 has never been evaluated in the catalytic conversion of 1-butene to 2-butene before because O_2 seemed to have no positive effect on the isomerization reaction. More importantly, oxidizing gases can react with butene at high temperatures to yield unwanted by-products. We

Fig. 4. Reasons for the decrease in catalytic activity. (a) The effects of sequential He and H_2 exposures are shown on the catalytic performance of a Pd/SNS catalyst at an O_2 :1-butene ratio of 1:1, (b) Pd 3d XPS spectra and (c) H_2 -TPR patterns of the Pd/SNS catalysts. Used catalysts are labeled with the reaction condition (for example, "25-O" refers to a reaction performed at 25°C in the presence of O_2), similarly hereinafter.

Fig. 5. Morphologies of Pd/SNS catalysts. (a and b) FE-SEM and HR-TEM micrographs of fresh Pd/SNS catalyst; (c–e) TEM micrographs of used Pd/SNS catalysts: (c) used 25, (d) used 25-O, and (e) used 50-O.

observed that the introduction of O_2 into the reaction mixture enhanced the degree of conversion of 1-butene to 47.6%. 2-Butene was the only detected product and no CO_2 was produced. Moreover, O_2 seemed to have no significant effect on the *trans*:*cis* ratio of 2-butene, so we hypothesize that O_2 activates the reaction without breaking C–C bonds or otherwise changing the reaction mechanism.

The effect of the O_2 :1-butene ratio was also evaluated, and the results are shown in Fig. 3b. When the ratio of O_2 :1-butene was 0.5:1, the yield increased to 57.2%. Then the catalytic performance decreases a little with higher O_2 :1-butene ratio.

3.4. Reasons for the decrease in catalytic activity

The activity of Pd/SNS catalyst somewhat decreased with reaction time. The transformation from a reductive to an oxidative valence in noble metals is thought to be one of the main causes for the deactivation of supported noble metal catalysts in heterogeneous reactions [35]. Fig. 4a showed the percent yield of 2-butene over 2 h with sequential exposure to helium (He) and hydrogen (H_2) at different temperatures. Catalytic activity was evaluated for an additional hour after each exposure. Exposure to He failed to reactivate the catalysts, which eliminated the possibility of trace surface water poisoning the catalyst. However, the catalyst was reactivated again when exposed to H_2 at lower temperatures. Other possible reasons for the observed decrease in catalytic activity, including Pd nanoparticles aggregation and carbon deposition, cannot be solved during these processes. Above

Fig. 6. Proposed reaction scheme for the isomerization of 1-butene to 2-butene over a Pd/SNS catalyst.

all, the oxidation of active sites is the primary reason for decreased catalytic activity.

Fig. 4b shows a Pd (3d) X-ray photoelectron spectrum (XPS) of a fresh Pd/SNS catalyst. Only Pd^0 ($3d_{3/2} = 341.6$ eV and $3d_{5/2} = 336.2$ eV) [36,37] was observed, suggesting that the Pd remained fully reduced during the preparation process. After the reaction, peaks corresponding to PdO appear, suggesting that Pd is partially oxidized. These peaks become more prominent when O_2 was added to the reaction feed gas. Fig. 4c shows the H_2 temperature-programmed reduction (H_2 -TPR) patterns of Pd/SNS catalyst. Compared with fresh Pd/SNS catalyst, broad peak emerges around 100 °C, which confirmed with the XPS results.

Table 1
Product distribution of different reaction gases over a Pd/SNS catalyst.

Reaction gas	Product distribution (%) ^a		
	1-Butene	<i>Trans</i> -2-butene	<i>Cis</i> -2-butene
1-Butene	63.0	26.1	10.9
<i>Trans</i> -2-butene	0	100	0
<i>Cis</i> -2-butene	0	0	100

^a The molar ratio of O₂:1-butene was 0:1 and the reaction temperature was 25 °C.

However, as shown in Fig. 4a, exposure to H₂ failed to fully restore catalytic activity. In addition, the accelerated decrease in activity in the presence of O₂ remains unexplained. To illustrate these problems, the morphologies of several Pd/SNS catalysts were studied by field-emission scanning electron microscopy (FE-SEM) and (HR-TEM), and the corresponding micrographs are shown in Fig. 5. As shown in Fig. 5a, the particle size of SNS is narrowly distributed (about 20 nm), which agrees with the D_{BET} data shown in Table S1. The SNS nanospheres were randomly arrayed in three dimensions, and the resulting disordered mesoporous framework provided an easy route for the diffusion of reactants and products [38,39], thereby facilitating catalytic activity. Fig. 5b shows the Pd nanoparticles of a fresh catalyst with an average diameter of about 1.7 nm. After running the reaction at 25 °C, the nanoparticles grew larger to about 2.1 nm, as shown in Fig. 5c. In Fig. 5d, the addition of O₂ further increased the degree of aggregation (2.8 nm), which led to a decrease in catalytic activity [35,40]. These results also imply that O₂ may accelerate nanoparticle aggregation during the reaction. In addition, the Pd nanoparticles grew to 3.1 nm after running the reaction at 50 °C, as shown in Fig. 5e. This explains the low catalytic activity observed at this slightly higher temperature.

3.5. Reaction process

Fig. 6 shows that the double-bond-shift isomerization of 1-butene is a single molecular reaction and generally involves the following four consecutive steps as reported [15,18,19,41–44]: (1) gaseous 1-butene adsorbs onto the surface of Pd nanoparticles, (2, 3) adsorbed 1-butene is converted to adsorbed 2-butene via a butenylcarbenium ion intermediate, and (4) 2-butene diffuses to the gas phase. Many researchers have reported a simple stepwise process for steps (2) and (3). First, butenylcarbenium ion intermediate is formed by abstraction of hydride, and then the anomeric carbon atom is attacked by the hydride to finish the catalytic cycle. During step (2), O species could promote the splitting of the C–H bond, and further facilitate the 1-butene double-bond-shift isomerization reaction [45,46]. We conclude that is the reason for the adding of O₂ could enhance the yield of 2-butene.

The stable conformers of gaseous 1-butene are *trans*- and *gauche*-type, with the methyl group eclipsing the C=C double bond or skewed from this position by about 120°, respectively [47,48]. Because of the free rotation of the C–C single bond, *trans*- and *gauche*-1-butene can freely interconvert in the gas phase with a *trans:gauche* ratio of about 1:2. Therefore, step (1) has no practical effect on the *trans:cis* ratio of the butenylcarbenium ion. In addition, geometric isomerization between *trans* and *cis* isomers is rare in the butenylcarbenium ion because of its extremely stable structure [25]. The data in Table 1 suggest that the titled reaction is irreversible and *trans*-2-butene or *cis*-2-butene does not transform into any isomer over Pd/SNS. Neither adsorbed nor gaseous 2-butene is free to convert between the *trans* and *cis* isomers, which is different from other catalytic systems [24,44]. In other words, after step (2), once the “flat” butenylcarbenium ion formed, the geometry of the carbon skeleton cannot be altered. Thus, the

geometry of the butenylcarbenium ion intermediate, which ultimately determines the final *cis:trans* ratio of the 2-butene product, must be determined during step (2).

Based on the above experiments and discussions, a reaction process for the isomerization of 1-butene to 2-butene over a Pd/SNS catalyst is proposed. Pd nanoparticles act as active sites for this irreversible reaction. 1-Butene is converted to 2-butene via a butenylcarbenium ion, and the *trans:cis* ratio of this ion determines the same ratio in the product. O₂ accelerates this reaction but does not fundamentally change the reaction mechanism.

4. Conclusions

An efficient and practical approach for the isomerization of 1-butene to 2-butene was realized at room temperature based on a silica nanospheres (SNS)-supported nano-Pd catalyst. This system exhibited a unique catalytic performance with no additional energy requirement. The yield of 2-butene was 37.0% at 25 °C, and the only detected product was 2-butene. Differs from previous reports, we found Pd⁺ was inactive at the same reaction condition. The addition of O₂ was shown to enhance the yield to 57.2% without the production of unwanted by-products such as CO₂.

The surface acidity of catalyst had remarkably influences on catalytic activity. The activity of a used catalyst could be recovered by exposure to H₂ gas and consequent reduction.

A reaction process was proposed in which reaction temperature influences the *trans:cis* ratio of a butenylcarbenium ion intermediate, which ultimately determines that of the 2-butene product.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.04.040>.

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