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
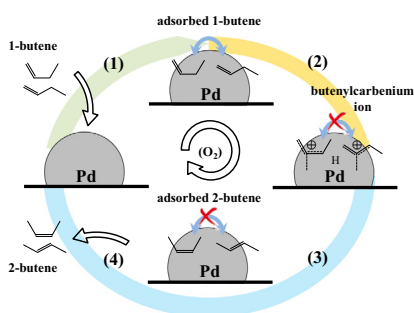
ABSTRACT

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 O_2 into the reaction mixture dramatically improved the yield efficiency to 57.2% without the formation of by-product CO_2. 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, Pd^0 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 C_4 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

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 date 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 CO_2 are also easy to generate, therefore studies about introducing oxygen (O_2) into the reaction mixture have been rare. Running the isomerization reaction at room temperature allows the effects of O_2 to be evaluated.

Perissinotto et al. [14] prepared a series of acid-leached metakaolin 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 °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, $[Pd(CH_3C–N)_4(BF)_2]$ and its tertiary phosphine derivatives as catalyst and CH_3CN or $CHCl_3$ were used as solvents. They found Pd^{2+} 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/TiO_2 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 Pd^0 nanoparticles were also efficient for the titled reaction at room temperature. Furthermore, this study explores the influences of surface acidity and O_2 on the double-bond-shift isomerization reaction.

2. Experimental section

2.1. Chemicals and materials

Palladium chloride ($PdCl_2$, Sinopharm Chemical Reagent Co., Ltd., AR), chloroauric acid ($HAuCl_4·4H_2O$, Sinopharm Chemical Reagent Co., Ltd., AR), and chloroplatinic acid ($H_2PtCl_6·6H_2O$, Sinopharm Chemical Reagent Co., Ltd., AR) were used as noble metal precursors.

Silica nanospheres (SNS, Aladdin Reagent Co., Ltd., 99.5%), Silicon dioxide (SiO_2, Degussa Co., Ltd., 99.8%), H-BEA zeolite (Nankai University Catalyst Co., Ltd.), ZSM-5 zeolite (Nankai University Catalyst Co., Ltd.), aluminum sesquioxide (Al_2O_3, Shandong Aluminum Co., Ltd.), and titanium dioxide nanopowder (TiO_2, Aladdin Reagent Co., Ltd., 99.5%) were selected as supports.

Sulfuric acid (H_2SO_4, 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 O_2 in N_2.

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 H_2 at 300 °C for 3 h, and then exposed in N_2 to remove residual H_2.

Pd/SNS and Pd/SiO_2 catalysts were also leached with acid aqueous solution for further study. The catalysts were soak in 1M H_2SO_4 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-H_2SO_4.

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 Al_2O_3 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:

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

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

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