

Kinetics and mechanism of double-bond isomerization of n-butenes over tungsten oxide supported on mesoporous silica SBA-15

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Introduction

It is of fundamental interest to investigate the mechanism of double-bond isomerization of n-butene over solid acid catalysts due to the simplicity of this acid-catalyzed reaction, which involves only cis/trans isomerization and double-bond shift. In previous work, kinetic and mechanistic investigation of double-bond isomerization of butenes has been conducted extensively on alumina and silica-alumina. Several mechanisms have been proposed primarily based on kinetics studies, including the classical carbonium ion[1], concerted hydrogen-switch[2], the combination/competition of the above two mechanisms[3] and π -complex mechanism[4]. It is obvious that all these postulations were derived from the product distribution (selectivity) in butene isomerization, and no direct evidence about the intermediates or reaction pathway has been reported yet.

In this work, we investigated the mechanism of double-bond isomerization over tungsten oxide supported on mesoporous-silica by reaction kinetics studies and density functional theory (DFT) calculations. From these results, we propose that butene isomerization over tungsten oxide proceeds via the formation of butoxide as intermediate, and the rate-determining step is the formation of butene from butoxide via a concerted mechanism.

Materials and Methods

A well-dispersed 30wt% $\text{WO}_x/\text{SBA-15}$ catalyst was prepared by a solution ALD (atomic layer deposition) method [5, 6] onto a SBA-15 support, and the final catalyst was calcined at 500°C for 1h. The kinetic measurements of the n-butene (trans-2-, cis-2-, 1-butene) isomerizations were carried out in a quartz fixed-bed reactor (1cm i.d.) at 105°C and atmospheric pressure, and the reaction gas consists of 0.1-0.5% butene and 0.1-0.7% H_2O with balance of He. The gas effluent from the reactor was analyzed by a gas chromatograph (HP 5890) equipped with flame ionization and thermal conductivity detectors. The reaction rates (TOF) were calculated based on the nominal WO_x site number in the catalyst. The apparent activation energies for butene isomerization were measured at 70-105°C. Theoretical calculations were carried out employing density functional theory (DFT) with a spin unrestricted gradient corrected functional for exchange and correlation as implemented in the CP2K package [7].

Results and Discussion

The three types of n-butenes, trans-2-, cis-2- and 1-butene, were found to reversibly interconvert between each other in parallel at 105°C. The rates of butene isomerization exhibit order dependency on butene of 0.63-0.83 and slight inhibition by water vapor. The apparent activation energies were in the range of 60-90kJ/mol. The kinetics of butene isomerization on

$\text{WO}_x/\text{SBA-15}$ was found to fit the Langmuir-Hinshelwood model and the rate-limiting step was determined to be the surface isomerization reaction. The primary selectivity for isomerization of 1-butene (1), trans-2-butene (t) and cis-2-butene (c), or the initial t/c, c/1 and t/1 was 0.64, 4.67 and 4.0, respectively, indicating that stereoselectivity (cis-preference) exists in isomerization of 1-butene to 2-butenes, and the cis/trans isomerization prevails over the double-bond shift in 2-butene isomerization. Consistent with prior literature, we propose a non-classical carbonium ion mechanism for double-bond isomerization over tungsten oxide. Furthermore, the exact nature of the transition states and intermediates involved in the reaction pathways were provided by detailed DFT calculations, which suggest that formation of alkoxy species is most likely to occur for all butenes, and that the rate determining step in these reactions will be the formation of alkene from alkoxy by a concerted mechanism (Fig.1). The energy barriers obtained from DFT are on the order of 90-120kJ/mol which is in reasonable agreement with those from kinetics experiments. In addition, the conventional carbocation mechanism and the concerted hydrogen-switch mechanism were ruled out from both DFT and kinetics results.

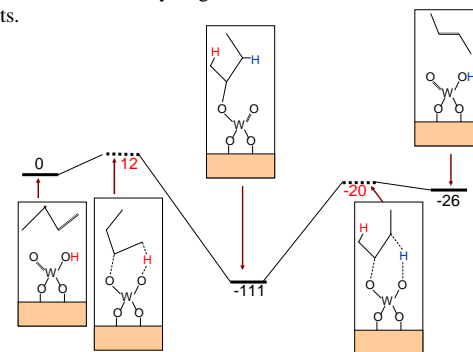


Figure 1. The energy landscape for 1-butene isomerization to trans-2-butene over $\text{WO}_x/\text{SBA-15}$ by DFT calculations. The unit of the values in the figure is in kJ/mol.

Significance

We report for the first time the mechanism of n-butene double-bond isomerization over supported tungsten oxide, using the combined kinetics and detailed DFT calculation approach.

References

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