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# Linoleic acid isomerization on $Ru/Al_2O_3$ catalyst
## 2. Elementary step mechanism and data fitting

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## Abstract

The selective double bond isomerization reaction of linoleic acid to *cis*-9,*trans*-11-conjugated linoleic acid and *trans*-10,*cis*-12-conjugated linoleic acid on commercial $H_2$-preactivated $Ru/Al_2O_3$ catalyst studied at 135–165 °C under kinetic control in a slurry reactor under atmospheric pressure in *n*-decane solution using the linoleic acid-to-surface ruthenium molar ratios 2.5, 5, and 10, was investigated by mathematical modeling. Over such catalyst and at the conditions used, the reaction scheme involves competitive isomerization of linoleic acid to conjugated linoleic acid isomers as well as hydrogenation of linoleic acid to oleic acid. These competing steps are through a complex relation strongly affected by chemisorbed hydrogen on the Ru surface. The concentrations of chemisorbed hydrogen and adsorbed key intermediates on the ruthenium surface influenced the catalytic activity and the selectivities toward isomerization and hydrogenation products through a complex relation. The isomerization rate was enhanced by catalyst preactivation under hydrogen, but increased hydrogen coverage on the Ru surface also restrained the isomerization selectivity. A reaction network and mechanism were advanced. Mechanistic models were developed from proposed elementary stage mechanism and corresponding kinetic equations were derived. Data fitting allowed discrimination between rival mechanistic models, more specifically the influence of hydrogen on the isomerization kinetics.

*Keywords:* Conjugated linoleic acid (CLA); $Ru/Al_2O_3$ catalyst; $H_2$-preactivation; Kinetic modeling; Double bond migration; Isomerization; Hydrogenation

## 1. Introduction

In the selective double bond isomerization reaction of linoleic acid to *cis*-9,*trans*-11-conjugated linoleic acid and *trans*-10,*cis*-12-conjugated linoleic acid (CLA) isomers over aluminium oxide supported ruthenium catalyst, one of linoleic acids two double bond migrates to form a conjugated system [1–6]. This is the second paper in the series aiming to investigate the kinetics of $Ru/Al_2O_3$ catalyzed linoleic acid isomerization at different conditions and to present a kinetic model, which is consistent with mechanistic data and observed kinetic regularities.

## 2. Catalytic surface reactions

Over supported metal catalysts [1–6], the reaction network involves six steps: (1) double bond migration of linoleic acid to conjugated linoleic acid, (2) positional and geometric isomerization of conjugated linoleic acid, (3) double bond hydrogenation of linoleic acid to mono-enoic acids, (4) double bond hydrogenation of conjugated linoleic acid to mono-enoic acids, (5) positional and geometric isomerization of mono-enoic acids, and (6) double bond hydrogenation of mono-enoic acids to stearic acid. In the following discussion, the term isomerization refers to double bond migration yielding a conjugated system. The sum of the overall isomerization selectivity and the hydrogenation selectivity is equal to unity.

A detailed description of the characterization of the $Ru/Al_2O_3$ catalyst by nitrogen adsorption, X-ray photoelectron spectroscopy, scanning electron microscopy-energy dispersive X-ray analysis, and temperature programmed desorption of hydrogen techniques as well as a detailed description of the linoleic acid

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**Nomenclature**

| | |
|---|---|
| $a$ | activity |
| $a_0$ | initial activity |
| **A** | linoleic acid |
| **B** | *cis*-9,*trans*-11-CLA |
| $c$ | concentration |
| $c$ | model constants |
| **C** | *trans*-10,*cis*-12-CLA |
| $C_{18}$ | 18 carbon atom fatty acids |
| $d$ | order of deactivation |
| **D** | *trans*-9,*trans*-11-CLA |
| **E** | *cis*-9,*cis*-11-CLA |
| $E_\mathrm{a}$ | activation energy |
| $E_\mathrm{d}$ | activation energy or temperature dependency of deactivation |
| H | hydrogen |
| $I$ | number of intermediates |
| $k$ | kinetic constant |
| $k_\mathrm{d}$ | deactivation constant |
| $k_\mathrm{d0}$ | frequency factor of deactivation |
| $k^0$ | pre-exponential/frequency factor |
| $K$ | equilibrium factor |
| **L** | oleic acid |
| $m$ | catalyst mass |
| $N(i)$ | independent basic route $i$ |
| $N$ | mole fraction |
| $N$ | number of basic routes |
| $p$ | pressure |
| $Q$ | conversion independent constant |
| $r$ | consumption/generation rate |
| $r_\mathrm{iso}$ | overall linoleic acid isomerization rate |
| $r_\mathrm{hydr}$ | linoleic acid hydrogenation rate |
| $-r_\mathrm{A}$ | rate at which the catalyst converts reactant **A** |
| $-r_\mathrm{A0}$ | rate of reaction of **A** with a fresh catalyst |
| $R$ | sum of kinetic constants $k_{11}$, $k_{12}$, $k_{13}$, $k_{14}$, and $k_{15}$ |
| $R^2$ | coefficient of determination |
| $R_\mathrm{gas}$ | the gas constant |
| $s$ | state of the system |
| $S$ | sum of kinetic constants $k_4$, $k_5$, $k_6$, $k_7$, and $k_8$ |
| $S$ | number of stages |
| SRS | sum of residual squares |
| $t$ | unit time |
| $T$ | reaction temperature |
| $T_\mathrm{mean}$ | mean temperature of the experiments |
| **U** | unknown CLA isomer |
| $w$ | weight matrix for observations |
| $W$ | number of balance equations |
| $x$ | design variables |
| $\overline{y}$ | average of data points |
| $y_\mathrm{p}$, | response variables |
| Z | vacant surface site for chemisorption of organic molecule |
| Z′ | vacant surface site for chemisorption of hydrogen |
| Z$i$ | chemisorbed compound $i$ |
| Z′H | chemisorbed hydrogen |
| ZI(1) | chemisorbed half-hydrogenated intermediates derived from **A** |
| ZI(2) | chemisorbed dehydrogenated intermediates derived from **A** |
| *Greek letters* | |
| $\Xi$ | chemical equilibrium |
| $\theta$ | estimated parameters |
| $\theta_i$ | fractional surface coverage of chemisorbed compound $i$ |
| $\theta_\mathrm{I(1)}$ | fractional surface coverage of chemisorbed half-hydrogenated intermediates derived from **A** |
| $\theta_\mathrm{I(2)}$ | fractional surface coverage of chemisorbed dehydrogenated intermediates derived from **A** |
| $\theta_0$ | fractional surface coverage of vacant sites |
| $\theta'_\mathrm{H}$ | fractional surface coverage of chemisorbed hydrogen |

isomerization, product analysis procedures and investigation of external and internal mass transfer are given in our previous report [7].

## 3. Mathematical modeling

### 3.1. Elementary step mechanism

The double bond migration reaction of linoleic acid to CLA over $H_2$-preactivated $Ru/Al_2O_3$ catalyst is thought to occur via the Horiuti–Polanyi mechanism [8] describing hydrogenation and isomerization of olefins. After the initial $H_2$-preactivation, linoleic acid is chemisorbed by the ruthenium surface. Thereafter, a hydrogen atom derived from a hydrogen-chemisorbed site is added to the chemisorbed acid to give a chemisorbed half-hydrogenated intermediate. If the hydrogen coverage on the catalyst surface is rather low, predominantly hydrogen abstraction by the metal takes place from an adjacent carbon atom, which might lead to a double bond migration depending from which carbon atom hydrogen is abstracted. If, on the other hand, the coverage of hydrogen is high, a second hydrogen atom is mainly added to the chemisorbed half-hydrogenated intermediate to result in a double bond hydrogenation. Free rotation of the half-hydrogenated intermediate, hydrogen abstraction, and desorption of the olefin result in *cis*/*trans*-isomerizations.

If, on the other hand, the first catalytic stage involves C–H bond cleavage, an allylic intermediate is formed on a supported metal atom or on an acidic site. Subsequent hydrogenation at a different carbon atom results in double bond migration [9].

Based on the obtained data, activity and selectivity can be treated separately. For further discussion, let us briefly analyze the reaction network and reaction kinetics. At present optimal conditions, the surface reaction network can be significantly simplified. As proposed in Fig. 1, linoleic acid undergoes isomerization to *cis*-9,*trans*-11-CLA, *trans*-10,*cis*-12-CLA, *trans*-9,*trans*-11-CLA, *cis*-9,*cis*-11-CLA, and an unknown