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Linoleic acid isomerization on Ru/Al_2O_3 catalyst 1: Conjugation and hydrogenation

Andreas Bernas, Dmitry Yu. Murzin*

Laboratory of Industrial Chemistry, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo/Turku, Finland

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Abstract

Selective double bond isomerization of linoleic acid to *cis*-9,*trans*-11-conjugated linoleic acid and *trans*-10,*cis*-12-conjugated linoleic acid on commercial non-preactivated and H_2-preactivated Ru/Al_2O_3 catalyst was studied under kinetic control in an agitated batch reactor (glass) at 135–165 °C under atmospheric pressure of nitrogen in *n*-decane solution. Catalyst characterization was done by nitrogen adsorption, X-ray photoelectron spectroscopy, scanning electron microscopy–energy dispersive X-ray analysis, and hydrogen temperature programmed desorption techniques. Over such catalyst, the network involves six reaction: (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 monoenoic acids, (4) double bond hydrogenation of conjugated linoleic acid to monoenoic acids, (5) positional and geometric isomerization of monoenoic acids, and (6) double bond hydrogenation of monoenoic acids to stearic acid. The concentrations of chemisorbed hydrogen and an adsorbed key intermediates on the ruthenium surface influenced the catalytic activity and the selectivities toward isomerization and hydrogenation products through a complex relation. Although presence of hydrogen promoted the side reaction double bond hydrogenation, the isomerization rate was enhanced by chemisorbed hydrogen.

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

1. Introduction

In the recent years, there has been an increased interest in applying heterogeneous catalysts to conventional organic reactions, which traditionally used to be performed under homogeneous conditions. One of the main obstacles to proper kinetic modeling of such chemical reactions catalyzed by solids is the too complicated reaction network with a large variety of formed products. Among these reactions is isomerization of linoleic acid (*cis*-9,*cis*-12-octadecadienoic acid) to conjugated linoleic acid (CLA). In the superficially simple selective double bond isomerization reaction of linoleic acid to *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers over aluminium oxide supported ruthenium catalyst, one of linoleic acids two double bond migrates to form a conjugated system.

Linoleic acid is a chief constituent of tall oil and vegetable oils [1] while CLA is found in meat and dairy products, especially those from ruminant sources where it is synthesized from linoleic acid by rumen bacteria. Positive health benefits are ascribed to the consumption of the *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers, which recently have been found to affect immunomodulation, body composition alteration, insulin sensitivity, and glucose tolerance, and they can prevent or cure atherosclerosis and stomach, colon, skin, and prostate cancer, and are thus of huge interest in food and health research [2–7]. Studies have demonstrated that the *cis*-9,*trans*-11-CLA isomer is responsible for the anticarcinogenic effects of CLA [2,3] while the *trans*-10,*cis*-12-CLA isomer produces the changes in body composition and is responsible for the antiatherogenetic effects. The dietary significance of the other isomers is unknown.

CLA, which was identified year 1987, is a collective term describing positional and geometric conjugated dienoic isomers of linoleic acid. Linoleic acid has double bonds located on carbons 9 and 12, both in the *cis* configuration, whereas CLA has either the *cis* or *trans* configuration or both located along the carbon chain. Twenty different CLA isomers have been identified through ^{13}C NMR, i.e. the *cis*,*cis*, *trans*,*trans*, *cis*,*trans*, and *trans*,*cis* isomers of the 7,9, 8,10, 9,11, 10,12, and 11,13-octadecadienoic acids [4].

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* Corresponding author. Tel.: +358 2 215 4985; fax: +358 2 215 4479.
E-mail addresses: abernas@abo.fi (A. Bernas), dmurzin@abo.fi (D.Yu. Murzin).

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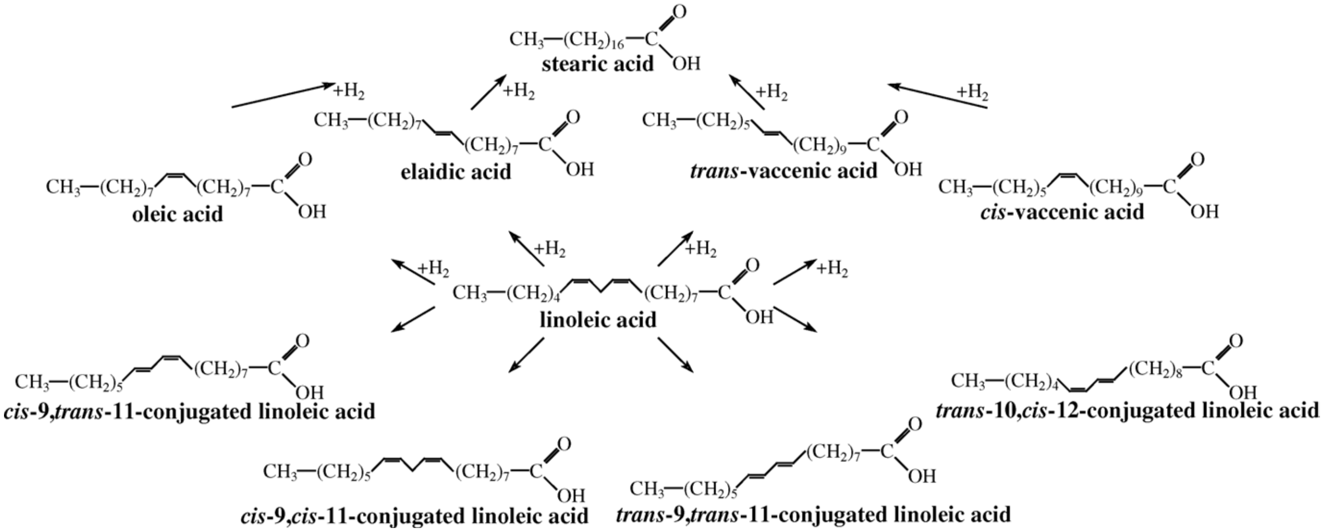

Fig. 1. Linoleic acid isomerization and hydrogenation network in presence of solid catalyst.

A recent innovation [8–12] has opened new dimensions for production of the anticarcinogenic and antioxidative *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers by isomerization of linoleic acid over supported ruthenium catalysts. A new and clean heterogeneously catalytic pathway for isomerization of linoleic acid has been developed, which due to greener chemistry is an attractive alternative to the traditional homogeneous [1] linoleic acid isomerization. As demonstrated in Fig. 1, the network of catalytic stages involves a rivalry between conjugation and double bond hydrogenation of linoleic acid. CLA isomers do also undergo isomerization steps as well as hydrogenation to monoenoic species. Further, isomerization of monoenoic acids occurs. As can be seen in the figure, the reaction network involves following steps: (1) double bond migration of linoleic acid to conjugated linoleic acid isomers, (2) double bond hydrogenation of linoleic acid to monoenoic acid isomers, and (3) double bond hydrogenation of monoenoic acid isomers to stearic acid. Moreover, there exists (4) double bond hydrogenation of conjugated linoleic acid isomers to monoenoic acid isomers, (5) positional and geometric isomerization of conjugated linoleic acid isomers, and (6) positional and geometric isomerization of monoenoic acid isomers. The main CLA compounds are the *cis*-9,*trans*-11-, *trans*-10,*cis*-12-, *cis*-9,*cis*-11-, and *trans*-9,*trans*-11-CLA isomers, at the same time several other conjugated dienoic isomers of linoleic acid are generated. The monoenoic compounds are the oleic, elaidic, *cis*- and *trans*-vaccenic acids. Among tested combinations of single- and bimetallic group VIII catalysts with carbon-, MCM-, Al_2O_3-, SiO_2-, MgO-, and zeolite-support materials [10], the single catalyst that shows a feasible selectivity to *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers (desired products) is Ru/Al_2O_3 [11].

The central challenge in the study of heterogeneous metal catalysts is to uncover the association between the physiochemical structure of the supported metal surface and its catalytic behavior. All dependences vacant for observation are prone to contribute to a better understanding of the surface kinetics in solid catalyzed system. The aim of the present series of papers is 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. Experimental

2.1. Nitrogen adsorption

Ru/Al_2O_3 catalyst of 5 wt% metal loading was supplied by Fluka (Switzerland). The BET specific surface area and the pore size distribution of the catalyst were measured with an automatic physisorption–chemisorption apparatus (Sorptometer 1900, Carlo Erba Instruments). The pore size distribution was calculated according to the Dollimore–Heal method.

2.2. X-ray photoelectron spectroscopy

Analysis of the Ru/Al_2O_3 catalyst by X-ray photoelectron spectroscopy (XPS) was utilized to examine the chemical composition and the degree of catalyst reduction. Before performing XPS, the catalyst sample was preactivated ex situ at 100 °C for 1 h including heating time under hydrogen (100%, AGA) flow of 100 ml/min in the test reactor in order to get the same state of reduction as in the catalytic experiments. Thereafter *n*-decane was fed into the reactor under stirring and the wet sample was charged into a special sample holder in order to avoid exposure to air. The measurements were carried out with a Perkin-Elmer PHI 5400 ESCA system equipped with a PE software. The spectra was excited by 1253.6 eV non-monochromatized Mg Kα X-rays with a total instrumental resolution of about 1 eV at an analyzer pass energy of 35.75 eV. The photoelectron emission angle was 30° relative to the sample surface normal. The pressure of the analyzer chamber was below 2×10^{-8} Torr during the measurements. The sample charging in the measurements caused a small constant energy shift for all spectral lines, and thus the binding energy scale was calibrated using C 1s (284.5 eV) line as a reference. In the analysis of the spectra, the background shape was subtracted by Shirley algorithm prior to fitting of the Voigt line shape for each peak in the spectra.

2.3. Scanning electron microscopy–energy dispersive X-ray analysis

The chemical composition, the metal loading, and the metal particle size distribution of the Ru/Al_2O_3 catalyst were analyzed by scanning electron microscopy (SEM-EDX) measurements using a LEO 1530 system equipped with a ThermoNORAN Vantage analyzer using an acceleration voltage of 15 keV and a take off angle of 34.4862°.

2.4. Temperature programmed desorption of hydrogen

The number of active surface ruthenium sites and the hydrogen adsorption capacity of the Ru/Al_2O_3 catalyst were investigated by temperature programmed desorption of hydrogen (H_2-TPD) using a volumetric flow apparatus (Autochem 2910, Micrometrics) with argon (100%, AGA) as a carrier gas. Since 100 °C was used as hydrogen preactivation temperature in the isomerization experiments, the catalyst was in the H_2-TPD measurements heated in situ to 100 °C with a heating rate of 10 °C/min under a 50 ml/min hydrogen (100%, AGA) flow, maintained at 100 °C for 1 h under the same hydrogen flow, and thereafter flushed at 100 °C with 15 ml/min argon for 20 min, in order to have the same physio-chemical state of the ruthenium surface as the catalyst under operating conditions. The hydrogen desorption heating rate was 10 °C/min from 100 to 600 °C and the sample was kept at 600 °C for 30 min. The analyses of the desorbed gases were performed continuously with a quadrupole mass spectrometer (QTMD, Carlo Erba Instruments). For quantitative measurements, the mass spectrometer was calibrated for the hydrogen signal.

2.5. Isomerization of linoleic acid

The linoleic acid isomerization experiments were conducted in an isothermal 200-ml completely back-mixed at atmospheric pressure operated batch reactor of glass, which was provided with a reflux condenser system and a heating jacket using silicone oil as a heat transfer fluid. Two hundered milligrams of reagent grade linoleic acid (99%, Fluka) and 70 ml of the solvent *n*-decane (95%, Sigma–Aldrich) were mixed and de-oxygenized by a nitrogen (100%, AGA) flow of 100 ml/min for 20 min in a separate bubbling unit. A quantity of 200, 400, or 800 mg of the Ru/Al_2O_3 catalyst was charged into the reactor and preactivated in situ at 100 °C for 1 h including heating time under a hydrogen (100%, AGA) flow of 100 ml/min in the absence of reactant and solvent. The linoleic acid-to-surface ruthenium molar ratios are therefore 10, 5, and 2.5, respectively. After the catalyst preactivation, nitrogen was fed through the reactor for 20 min to get an inert atmosphere while heating the system to the reaction temperature of 135–165 °C. The reactant solution was introduced into the reactor under stirring. The reaction time was initialized to zero as soon as the liquid phase came in contact with the catalyst. A nitrogen flow was fed through the reactor during the isomerization to have an inert atmosphere and the reactor outlet was locked by a fluid to prevent back-diffusion of oxygen into the reactor. The course of the reaction was followed by withdrawing samples smaller than 1 ml out of a total of 70 ml from the mixture periodically through a 0.5 μm catalyst filter to await analysis by gas chromatography, hence the liquid-to-catalyst ratio was decreasing with time. The temperature of the reflux condensers cooling medium was set to −20 °C and stirring baffles were used inside the reactor. The conditions above were chosen since (a) catalyst preactivation under hydrogen generates chemisorbed dissociated hydrogen sites on the ruthenium surface which in turn enhances the isomerization rate [8–12], (b) a catalyst activation temperature of 100 °C in enough to completely reduce ruthenium into the metallic state [13], (c) a reaction temperature lower than 145 °C increases the coverage of chemisorbed hydrogen on the ruthenium which in turn increases the selectivity toward double bond hydrogenation of linoleic acid and CLA isomers consecutively proceeding via monoenoic acids to stearic acid [11], and (d) the isomerization selectivity is optimized by the use of non-polar solvents such as *n*-nonane and *n*-decane [11]. The system was agitated at a stirring rate of 800 rpm to keep the catalyst uniformly dispersed in the reaction medium and to eliminate effects of external mass-transfer, which was verified by comparing reaction rates at varied agitation rates and catalyst quantities, otherwise using the same reaction conditions. The isomerization was tested at different ranges of catalyst particle size intervals to elucidate possible limitations by internal pore diffusion in the catalyst particle on reaction rates.

2.6. Analyses

The samples from the reactor were silylated by using the reagents *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS), both supplied by Acros Organics, and analyzed by a gas chromatograph (GC, Hewlett-Packard 6890 Series) equipped a 25 m HP-5 column (inner diameter: 0.20 mm and film thickness: 0.11 μm), flame ionization detector (FID) unit, and an autosampler injector. The silylation operations were conveniently performed with the entire series of samples from each isomerization reaction in parallel to avoid effects of decomposition. A detailed description on the silylation procedure is given in separate papers [9–11]. Peaks identities were verified by a gas chromatograph–mass spectrometer system (GC/MS, Hewlett-Packard) applying the same GC conditions.

3. Results

3.1. Catalyst characterization

3.1.1. Physical properties of Ru/Al_2O_3 catalyst

The Ru/Al_2O_3 catalyst can be described as a powder consisting of catalyst particles sizes smaller than 63 μm, which was measured by sieving. The BET specific surface area was 129 m^2/g as determined by nitrogen adsorption. Approximately,

Table 1
Analyses of chemical composition of Ru/Al_2O_3 catalyst by XPS and SEM-EDX

Element	XPS (at.%/wt%)	SEM-EDX (at.%/wt%)
Ru	2.5/11.5	1.2/6.2
Al	33.0/41.0	27.7/37.2
O	64.5/47.4	71.1/56.6

20% of the relative pore volumes of Ru/Al_2O_3 were within the pore size interval 10.0–100.0 nm, 7% within 5.0–10.0 nm, 49% within 2.0–5.0 nm, 13% within 1.5–2.0 nm, and 11% within the interval 1.0–1.5 nm. Moreover, a small fraction of 0.6% of the relative pore volume lied within the interval 0.9–1.0 nm.

3.1.2. XPS and SEM-EDX

An estimation of the atomic composition of the Ru/Al_2O_3 catalyst, which was analyzed by XPS and SEM-EDX techniques, is given in Table 1. The magnitude of deviations of the aluminium-to-oxygen ratio of the sample from 2/3 gives an idea of the accuracy of the measurements made by the two techniques. In the SEM-EDX analyses, the atomic Ru/Al ratio was estimated to be 1:27. The electron diffraction indicated a chemical composition of 27.7 at.% of Al, 71.07% of O, and 1.23% of Ru, hence the mass related fraction of Ru was according to the SEM-EDX measurements 6.2 wt%. As analyzed by XPS, the Ru $3d_{5/2}$ spectra of the sample signified that the metallic state of Ru was dominating.

The catalyst had a rather wide metal particle size distribution. Scanning electron micrographs of the Ru/Al_2O_3 catalyst with magnifications ×100 and ×30,000 are shown in Fig. 2. According to the figure, a majority of the ruthenium crystals of the catalyst were very dispersed with sizes down to some 10 nm, hence the main part of the Ru crystals are located inside the pores of Al_2O_3 although larger agglomerates of metal also were found, but it should be kept in mind that the actual metal particle size distribution is such that by no means SEM can account for it, even using a magnification of ×30,000.

3.1.3. H_2-TPD

Fig. 3 demonstrates the H_2-TPD pattern of the Ru/Al_2O_3 catalyst, which showed a maximum hydrogen desorption rate already at a temperature of 110 °C which is a rather lower value of the maximum hydrogen desorption temperature, indicating that weakly chemisorbed and thus relatively reactive hydrogen is involved. The hydrogen uptake was obtained by numerical integration of the area under the H_2-TPD curve. The hydrogen adsorption capability was 1.77×10^{-4} mol H_2/g catalyst (related to the total catalyst mass) or 2.86×10^{-3} mol H_2/g Ru (related to the metal mass of 6.2 wt% as analyzed by SEM-EDX). Thus the number of active surface ruthenium atoms per total number of ruthenium atoms, i.e. dispersion, is 0.58. Numerical integration of the area from 165 to 600 °C indicates that up to 62% of the total amount of chemisorbed hydrogen will remain on the ruthenium surface after an increase of the temperature to the typical reaction temperature used (165 °C) if there is no competitive adsorption of other compounds.

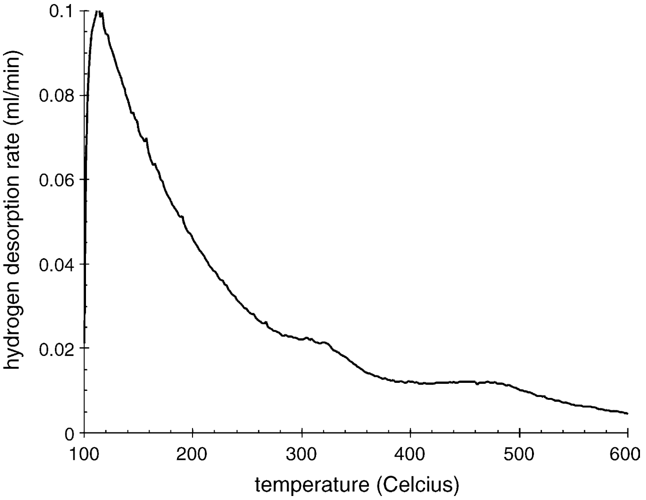

Fig. 3. H_2-TPD pattern of Ru/Al_2O_3 catalyst.

3.2. Mass transfer

3.2.1. External diffusion

Activity and selectivity data on Ru/Al_2O_3 catalyst in isomerization of linoleic acid to conjugated linoleic acid is reported in Table 2. Because of the relatively high bulk density of Ru/Al_2O_3, the reaction was conducted at 165 °C at varied stirring rates

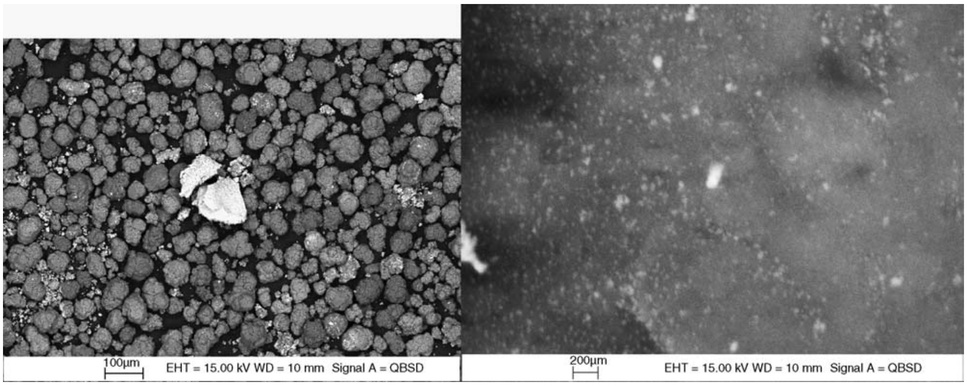

Fig. 2. SEM micrographs of Ru/Al_2O_3 with magnifications ×100 and ×30,000.

Table 2
Activity and selectivity data on Ru/Al_2O_3 catalyst in linoleic acid isomerization

No.	Stirring rate (rpm)	Catalyst mass (g)	Catalyst particle diameter interval (μm)	Reaction temperature (°C)	Conversion[a]	S_I[b]	S_D[c]	Initial overall reaction rate ($10^{-5}\ s^{-1}$)[d]	TOF ($10^{-4}\ s^{-1}$)[e]
1	200	0.8	0–63	165	0.26	0.83	0.52	1.84	0.60
2	500	0.8	0–63	165	0.44	0.85	0.54	4.28	1.02
3	800	0.8	0–63	165	0.45	0.87	0.59	4.42	1.05
4	1600	0.8	0–63	165	0.44	0.87	0.60	4.53	1.02
5	800	0.4	0–63	165	0.35	0.92	0.69	6.70	1.63
6	800	0.2	0–63	165	0.23	0.89	0.58	11.15	2.14
7	800	0.8	0–45	165	0.35	0.87	0.59	3.46	0.81
8	800	0.8	45–63	165	0.35	0.88	0.60	2.77	0.81
9	800	0.8	0–63	155	0.49	0.84	0.54	5.01	1.14
10	800	0.8	0–63	145	0.26	0.87	0.60	2.22	0.60
11	800	0.8	0–63	135	0.23	0.80	0.47	3.41	0.53

Note: Conditions—raw material, 0.2 g of reagent grade linoleic acid; solvent, 70 ml of *n*-decane; catalyst metal loading, 6.2 wt%; H_2-preactivation temperature, 100 °C; H_2-preactivation time, 1 h; reaction pressure, 1 atm of nitrogen; reaction time, 3 h.

[a] Total conversion of linoleic acid after 3 h.

[b] Selectivity toward isomerization at 30% conversion. S_I = mole fraction of all CLA isomers at 30% conversion/0.3.

[c] Selectivity towards desired CLA isomers at 30% conversion. S_D = mole fraction of *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers at 30% conversion/0.3.

[d] Initial overall reaction rate = total moles of linoleic acid converted after 30 min per unit time and moles of active surface ruthenium sites.

[e] Turnover frequency. TOF = total moles of linoleic acid converted after 3 h per unit time and moles of active surface ruthenium sites.

(Table 2, entries 1–4) and catalyst quantities (Table 2, entries 3, 5, and 6), otherwise using the same reaction conditions, in order to verify the influence of external mass transport. It was visually confirmed that the catalyst particles were lifted from the bottom of the glass reactor already at a stirring rate of 500 rpm and no changes in the dark color of the reaction medium were observed after further agitation increases. As, demonstrated in Table 2 and Fig. 4, the overall reaction rate and the conversion were higher for stirring rates 500–1600 rpm, at which the catalyst was dispersed in the liquid medium, than those for 200 rpm, at which the catalyst stayed at the reactor bottom. The reaction rate and the conversion at any reaction time kept constant values as the stirring rate was increased from 500 to 1600 rpm and as the catalyst mass was increased from 0.2 g via 0.4 g to 0.8 g. The selectivities were not significantly affected when stirring rate and catalyst mass were varied.

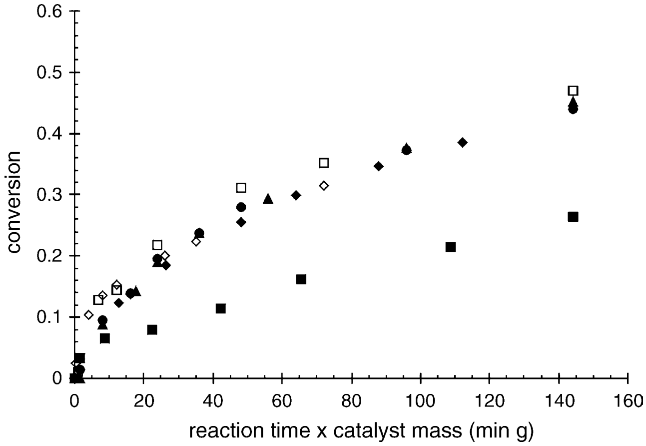

Fig. 4. Conversion of linoleic acid versus time multiplied by catalyst mass dependence at varied agitation rate and catalyst quantity for linoleic acid isomerization over $RuAl_2O_3$. (■) = 200/0.8, (◆) = 500/0.8, (▲) = 800/0.8, (●) = 1600/0.8, (□) = 800/0.4, (◇) = 800/0.2 rpm/g. *Conditions*: raw material, 0.2 g of reagent grade linoleic acid; solvent, 70 ml of *n*-decane; catalyst metal loading, 6.2 wt%; catalyst particle diameter interval, 0–63 μm; reaction temperature, 165 °C; H_2-preactivation temperature, 100 °C; H_2-preactivation time, 1 h; reaction pressure, 1 atm of nitrogen; reaction time, 6 h.

It can thus be concluded that external diffusion, caused either by poor mixing of the reaction medium or by catalyst mass fractions with larger particle diameter present on the bottom of the reactor, does not affect catalytic activity or selectivity at agitation rates above 500 rpm. Consequently the system was agitated at 800 rpm in all further isomerization experiments to eliminate effects of external transport of linoleic acid to the outer surface of the catalyst particles on reaction rates and to keep the catalysts uniformly dispersed in the reaction medium.

3.2.2. *Internal diffusion*

The influence of internal diffusion [14] was negligible. Rate limitation from resistance of internal diffusion of reactant and products was investigated by performing experiments over H_2-preactivated Ru/Al_2O_3 samples with two different particle size intervals at 165 °C (Table 2, entries 7 and 8). An identical conversion versus time dependence, the same turnover frequency (TOF, based on total moles of linoleic acid converted after 3 h per unit time and moles of active surface ruthenium sites) at 3 h of $0.81 \times 10^{-4}\ s^{-1}$, as well as similar selectivities of 88% toward the overall isomerization reaction and 60% toward the desired CLA isomers (since selectivities vary with conversion, selectivities are compared below at the same conversion level) were obtained when the catalyst particle size interval was changed from 0–45 to 45–63 μm, hence the observed rate is considered to be the intrinsic rate. It is therefore clear that the reactor is operating in the chemical regime at the plateau of the initial rate versus catalyst particle diameter dependence with the effectiveness factor one.

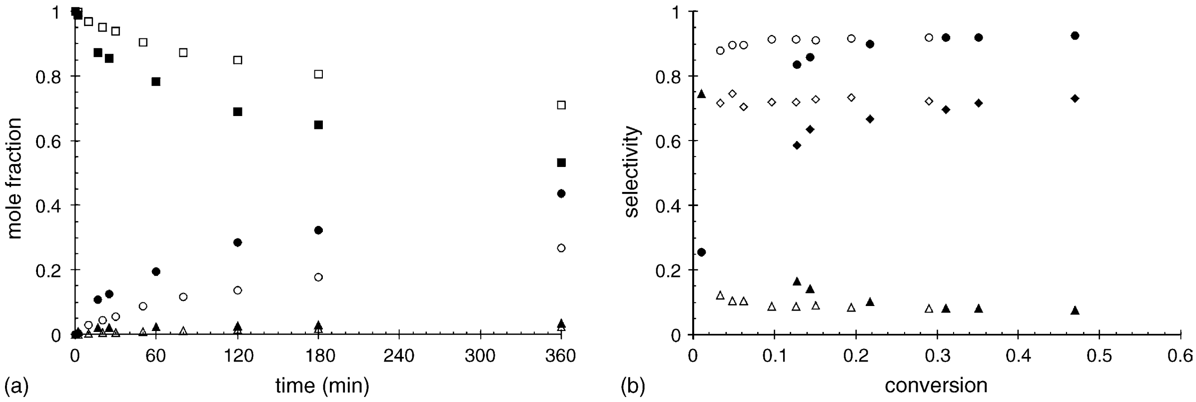

Fig. 5. Effect of catalyst preactivation hydrogen on (a) rate and (b) selectivity in linoleic acid isomerization over Ru/Al_2O_3. (■) linoleic acid; (●) CLA; (▲) hydrogenation products (monoenoic acids and stearic acid); (◆) *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA; open, no preactivation; filled, H_2-preactivated catalyst. Catalyst mass, 0.4 g; stirring rate, 800 rpm. Other conditions same as in Fig. 4.

3.3. Activity

Fig. 5(a) shows the fatty acid mole composition versus time dependence in isomerization of linoleic acid to conjugated linoleic acid isomers catalyzed by non-preactivated and H_2-preactivated aluminium oxide supported ruthenium catalyst at 165 °C. The mole fractions in the figures refer to the concentrations of the specific C_{18} compounds relative to the total concentration of C_{18} compounds, where C_{18} denotes 18 carbon fatty acids. The TOF at 3 h and the initial overall reaction rate (based on total moles of linoleic acid converted after 30 min per unit time and moles of active surface ruthenium sites) increased from 0.46×10^{-4} and 0.87×10^{-4} to 1.05×10^{-4} and $2.65 \times 10^{-4}\,s^{-1}$, respectively, when the Ru/Al_2O_3 catalyst was preactivated under a hydrogen atmosphere for 1 h at 100 °C.

After a reaction time of 6 h the linoleic acid consumption rate approaches zero. The composition at this point is through a complex connection influenced by: (i) the H_2-preactivation temperature and thereby the total amount of chemisorbed H_2 generated in the H_2-preactivation step, (ii) the reaction temperature that also affects the H_2-coverage on the ruthenium surface as predicted by the adsorption isotherm, (iii) the availability of vacant sites for linoleic acid adsorption on the ruthenium surface, (iv) competitive adsorption of linoleic acid, solvent, and reaction products, (v) deactivation of the catalyst, and (vi) the equilibrium composition.

3.4. Selectivity

The isomerization properties of several supported metal catalysts have been evaluated with reagent grade (99%) linoleic acid in a previous report [10]. Investigated catalysts were Ru, Ni, Pt, Pd, Rh, Ir, Os, and bimetallic Pt-Rh supported by activated carbon, Al_2O_3, SiO_2, $SiO_2Al_2O_3$, MCM-22, H-MCM-41, Y and β zeolites. It was concluded that Ru, Ni, and Pt have good properties for isomerization of linoleic acid. The activity and the isomerization selectivity were sensitive to the surface structure and hydrogen adsorption capacity of the metal–support combination. Metals with high hydrogen storage capacity such as Pd showed high activity and high selectivity for the double bond hydrogenation reaction, whereas most of the other metals, especially Ru favored double bond migration. The Ru metals activity for isomerization is to be expected from the fact that it has vacant d-orbitals, which can interact with π bonds of fatty acids as well as activating an adjacent C–H bond, which is a necessary step for a double bond migration. Very few catalysts, including Ru/C and Ru/Al_2O_3 [11], exhibit feasible conversion and reasonable selectivity toward the desired products *cis*-9,*trans*-11- and *trans*-10,*cis*-12-conjugated linoleic acid isomers and, which also is very important, low selectivity toward several non-desired conjugated dienoic isomers, especially the *trans*-9,*trans*-11-conjugated linoleic acid isomer. The single catalyst giving feasible conversion and reasonable selectivity toward the desired products *cis*-9,*trans*-11- and *trans*-10,*cis*-12-conjugated linoleic acid isomers and low selectivity toward several non-desired conjugated dienoic isomers is aluminium oxide supported ruthenium. In addition, the deactivation of Ru/Al_2O_3 and Ru/C was very slow compared to the rapid deactivation of zeolites, giving a reason for selecting Al_2O_3 and carbon supported Ru catalysts for further studies.

The Ru/Al_2O_3 catalyst showed relatively high selectivity toward the *cis*-9,*trans*-11- and *trans*-10,*cis*-12 isomers of CLA (desired products). When the isomerization was conducted at 165 °C in *n*-decane solution over Ru/Al_2O_3 previously preactivated under a hydrogen atmosphere as shown in Fig. 5(a), the 6 h sample included linoleic acid, monoenoic acids, stearic acid, *cis*-9,*trans*-11-, *trans*-10,*cis*-12-, *trans*-9,*trans*-11-, and *cis*-9,*cis*-11-CLA isomers, and one unknown CLA isomer. The fatty acid composition comprised 40 mol% of linoleic acid, 6 mol% of monoenoic acids, 0.4 mol% of stearic acid, and as much as 54% of CLA isomers. The CLA isomer distribution was 40 mol% of *cis*-9,*trans*-11-CLA, 29 mol% of *trans*-10,*cis*-12-CLA, 16 mol% of *trans*-9,*trans*-11-CLA, and 4 mol% of *cis*-9,*cis*-11-CLA, while the remaining 11 mol% consisted of one single unknown isomer. The selectivities toward specific isomers of CLA did not depend on the reaction time or the conversion. The distributions of specific conjugated linoleic acid isomers at 30% conversion in isomerization of linoleic acid over Ru/Al_2O_3 at 135–165 °C are given in Table 3. The CLA composition obtained at varied reaction temperature is quite regular and

Table 3
Distribution of specific conjugated linoleic acid isomers at 30% conversion in isomerization of linoleic acid on Ru/Al_2O_3 catalyst

Reaction temperature (°C)	Composition (mol%)				
	cis-9,*trans*-11-CLA	*trans*-10,*cis*-12-CLA	*trans*-9,*trans*-11-CLA	*cis*-9,*cis*-11-CLA	Other CLA isomers
135	34.4	24.4	21.2	5.4	13.8
145	44.6	24.9	15.4	3.7	11.4
155	39.8	25.2	15.6	4.3	15.2
165	39.6	29.0	15.9	4.4	11.2

Note: Conditions same as in Table 2.

it can be concluded that the ratios between the generation rates of the main isomers are fairly constant. The *cis*-9,*trans*-11-CLA isomer is the chief constituent followed by *trans*-10,*cis*-12-CLA, *trans*-9,*trans*-11-CLA, and *cis*-9,*cis*-11-CLA at any temperature.

The general trend of the linoleic acid isomerization over H_2-preactivated Ru/Al_2O_3 in an *n*-decane solution is a modest linoleic acid concentration decrease versus time and a generation of CLA isomers as main reaction products. Polymerization, cracking, or skeletal isomerizations of fatty acids were not observed at these conditions. Over similar catalysts [8–12,15], 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 monoenoic acids, (4) double bond hydrogenation of conjugated linoleic acid to monoenoic acids, (5) positional and geometric isomerization of monoenoic acids, and (6) double bond hydrogenation of monoenoic 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.

As a typical behavior for isomerizations on H_2-preactivated Ru/Al_2O_3 catalyst, it was observed that the concentrations of monoenoic acids and stearic acid are at the beginning of the reaction initially slightly increasing and approaching a stable value of a few mol%, while the CLA concentration continuously increases with time. Therefore, the isomerization selectivity is increasing and the hydrogenation selectivity is decreasing with conversion, as demonstrated in Fig. 5(b), indicating that the coverage of chemisorbed hydrogen on the ruthenium surface, which decreases during the reaction, affects the isomerization and hydrogenation rates. The availability of hydrogen and the activation temperature used in the preactivation step as well as the reaction temperature influence the hydrogen coverage on the catalyst surface. This, in turn, affects the activity and selectivity pattern. When the coverage of hydrogen is high, the linoleic acid hydrogenation consecutively proceeding via monounsaturated acids to stearic acid increases. When, on the other hand, the concentration of chemisorbed hydrogen is low (as at the end of the reaction when most of the preadsorbed hydrogen has been consumed), isomerization is preferred over hydrogenation. As demonstrated in Fig. 5(b), the selectivity toward *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers versus conversion dependence approximately followed the same pattern as the overall isomerization selectivity. For H_2-preactivated Ru/Al_2O_3, the selectivity to the desired isomers increased with conversion, since some H_2 chemisorbed on the metal surface initially is consumed for double bond hydrogenation. The non-preactivated Ru/Al_2O_3 catalyst showed a constant selectivity of 70% toward the desired products.

When 7.13×10^{-4} mol of linoleic acid was isomerized over the H_2-preactivated $RuAl_2O_3$ catalyst (Table 2, entry 3), the 6 h sample contained 4.05×10^{-5} mol of monoenoic acids and 0.32×10^{-6} mol of stearic acid. The amount of H_2 required for this hydrogenation is 4.67×10^{-5} mol. At 165 °C, the catalyst is capable of storing 1.42×10^{-4} mol of H_2 according to the H_2-TPD measurements, which is in reasonable agreement with observed hydrogenation. Speaking in terms of approximate estimations, the fraction of H_2 required for the observed hydrogenation reaction from the overall estimated adsorbed amount of H_2 is equal to 0.20. The remaining amount of chemisorbed hydrogen assists the double bond migration and *cis*/*trans*-isomerization reactions.

3.5. Influence of reaction temperature

Experiments were conducted over H_2-preactivated Ru/Al_2O_3 samples in *n*-decane solution at varied temperature levels in order to evaluate the required reaction temperature for keeping a feasible isomerization selectivity as rate and selectivity are dependent on the coverage of chemisorbed hydrogen on the ruthenium surface, which in turn is strongly influenced by the temperature. The initial rate decreased from 2.05×10^{-4} to $1.33 \times 10^{-4}\,s^{-1}$ when the reaction temperature was increased from 135 to 145 °C, because at a lower temperature level, more chemisorbed hydrogen is stored on the metal surface and this will enhance the isomerization rate (Table 2, entries 10 and 11). Moreover, the initial rate increased to $3.01 \times 10^{-4}\,s^{-1}$ when the reaction temperature was elevated to 155 °C (Table 2, entry 9) and stayed at this level for further increases of the temperature. The TOF after 3 h was first slightly increasing with temperature. As the reaction temperature was elevated from 135 °C via 145 °C to 155 °C, the TOF increased from $0.53 \times 10^{-4}\,s^{-1}$ via $0.60 \times 10^{-4}\,s^{-1}$ to $1.14 \times 10^{-4}\,s^{-1}$, correspondingly, and stayed at this level after a further increase of the temperature to 165 °C (Table 2, entries 3 and 9–11). At 135 °C, the overall isomerization selectivity at 30% conversion was lower, i.e. 80%, than at temperatures over 145 °C where the isomerization selectivity remained at 87% in all experiments, which indicates that 145 °C is the lowest temperature limit for an optimization of rate and selectivity by manipulating the hydrogen coverage of the metal surface.

3.6. *Influence of catalyst deactivation*

Let us clearly point out the main shortcoming of the investigated Ru/Al_2O_3 catalyst, which is a process related one. In addition to the observed reactions, the catalyst, as every catalyst used in vegetable oil related processes, *badly* deactivates. Although using very low linoleic acid-to-surface ruthenium molar ratios of 2.5, 5, and, 10, the activity was halved in a second reuse.

Deactivation of the Ru/Al_2O_3 catalysts was investigated by performing consecutive experiments over the same catalyst sample. After the experiment, the catalyst was separated from the fatty acid solution by vacuum filtration, washed with acetone in a stirred tank, dried overnight at 100 °C, and reduced at 400 °C for 4 h under hydrogen. In the second run, the isomerization selectivity at 30% conversion remained at approximately 90% while conversion, initial rate, and TOF at 3 h, approximately decreased by a factor of two. Despite deactivation, the selectivity at 30% conversion towards *cis*-9,*trans*-11-CLA and *trans*-10,*cis*-12-CLA was not strongly affected. The BET specific surface area kept a constant value of 160 m^2/g as the Ru/Al_2O_3 catalyst was being used and regenerated twice. The pore volume distribution was also not affected hence the reason for the observed deactivation lies within fouling of the active ruthenium sites or poisoning rather than irreversible plugging of pores by the heavy fatty acid molecules.

4. Discussion

4.1. *Metal–support interactions*

In solid catalyzed isomerization of linoleic acid to CLA, formation of the undesired *trans*-9,*trans*-11-CLA isomer represents a central difficulty, as *trans*-9,*trans*-11-CLA is the most thermodynamically stable form, which was concluded from special isomerization experiments using CLA isomers as reactants over Ru/C catalyst [11]. Several positional and geometric conjugated dienoic isomers are formed as intermediates in the consecutive isomerization starting from linoleic acid (*cis*-9,*cis*-12- form) to *trans*-9,*trans*-11-CLA. When CLA isomers were used as reactants over Ru/Al_2O_3 and Ru/C catalysts, the equilibrium sample did not contain any trace of linoleic acid. In general, the concentrations of the desired *cis*-9,*trans*-11-CLA and *trans*-10,*cis*-12-CLA isomers are initially increasing and as in a typical consecutive reaction decreasing after reaching a maximum value. Not only *trans*-9,*trans*-11-CLA, but also *cis*-9,*cis*-11-CLA and other unknown CLA isomers, start to build up later than the desired isomers. As described earlier, in our investigation [10] of single- and bimetallic group VIII metals on carbon-, MCM-41, MCM-22, Al_2O_3, SiO_2, MgO, and zeolite supports, Ru, Ni, and Pt showed feasible isomerization selectivity and Pd favored hydrogenation. No isomerization occurred over SiO_2 and MgO supported metal catalysts. Ru/H-MCM-41, Ru/H-Y, Ru/H-β, Ni/H-MCM-41, Ni/MCM-22, Ni/H-Y, Ni/H-β, and Pt/H-Y catalysts showed a very similar pattern, i.e. low conversion, wide product distribution, rapid deactivation, high selectivity toward to *trans*-9,*trans*-11-CLA, and non-existent selectivity to the desired CLA isomers. Ru/Al_2O_3 is the only investigated metal support combination that does not show a decreasing selectivity to the desired product with conversion [11].

4.2. *Mechanism*

Speaking in terms of molecular mechanisms, the double bond migration reaction of linoleic acid to CLA over a solid catalyst is thought to take place through several routes. The isomerization over H_2-preactivated Ru/Al_2O_3 catalyst could occur predominantly via the Horiuti–Polanyi mechanism [16] 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. The role of the Horiuti–Polanyi mechanism in isomerization of butenes was investigated by Touroude and Gault [17] by studying the deuterium distribution of exchanged and isomerized olefins obtained from *cis*-butene, *trans*-butene, and but-1-ene on iron films in presence of perdeuteropropene.

Moreover, if the first catalytic stage involves methylene 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.

Acid catalyzed isomerization may occur over oxidic metal sites. If linoleic acid adsorbs molecularly, it forms a π complex on the surface, with a C=C bond coordinated to a Lewis acid site. If Brønsted acid sites are present, protonation of linoleic acid can occur, resulting in a carbenium ion intermediate where the C=C character has been lost. Subsequent loss of a proton from another carbon atom results in double bond migration [18].

The mechanism of selective isomerization of linoleic acid into *cis*-9,*trans*-11- and *trans*-10,*cis*-12-conjugated linoleic acid isomers over ruthenium catalyst supported by aluminium oxide can proceed via parallell routes: apparently the double bond isomerization predominantly occurs both via the Horiuti–Polanyi mechanism, where hydrogen takes part as an astoichiometric component by hydrogen addition followed by hydrogen abstraction, and via an allylic mechanism, where hydrogen abstraction is followed by hydrogen addition.

Formation of conjugated linoleic acid isomers is thought to occur via several pathways. Most probably, the dienoic acids are chemisorbed in the di-ene adsorption mode followed by positional or *cis*/*trans* isomerization of one double bond of the carbon chain, whereas the other double bond is locked in its original position. A second possibility, that the acids are chemisorbed via the di-ene adsorption mode followed by positional or *cis*/*trans* isomerization of both double bonds cannot be ruled out. It is reasonable to assume that isomerization of the *cis*-12-double bond to the *trans*-11-bond (keeping the *cis*-9-bond locked) proceeds to *cis*-9,*trans*-11-CLA from *cis*-9,*cis*-12-linoleic acid in one step. Similarly, the reaction of *cis*-9,*cis*-12-linoleic acid to *trans*-10,*cis*-12-CLA by isomerization of the *cis*-9-bond to the *trans*-10-bond while keeping the *cis*-12-bond locked occurs in one step. When the concentration of linoleic acid decreases and the concentration of *cis*-9,*trans*-11- form increases, the latter one reacts to the most thermodynamically stable *trans*-9,*trans*-11- form in one single step by geometric isomerization of the *cis*-9-bond to the *trans*-9-bond whereas the *trans*-11-bond is locked. It is clear from kinetic runs [11], that isomerization of linoleic acid to *trans*-9,*trans*-11-CLA occurs consecutively in two steps via *cis*-9,*trans*-11-CLA and in addition, no trace of the *trans*-9,*cis*-11-CLA isomer was detected. The contribution of the second mechanism, in which the olefin undergoes adsorption in the di-ene adsorption mode, positional isomerization of both the double bonds, and desorption, was masked as the *trans*-10,*cis*-12-CLA isomer mainly reacted to the *cis*-9,*trans*-11-, *trans*-10,*cis*-12-, and *trans*-9,*trans*-11-CLA isomers [11].

A mechanism involving hydride transfer could also be operative. Hydride transfer from the solvent has been discussed in literature [19] in the case of isomerization of methyl linoleate (the methyl ester of linoleic acid) on carbon supported ruthenium catalyst. Moreover, hydride transfer reactions, in which the olefin itself acts as a hydrogen donor, might take place on acidic catalysts in the case of hydrocarbons [20]. In the literature, such a step, where chemisorbed methyl linoleate reacts to two hydrogen chemisorbed sites plus coke, has been proposed to explain the isomerization kinetics of methyl linoleate on aluminium oxide supported bimetallic ruthenium-nickel catalyst [21]. Hydride transfer might be one of the explanations for linoleic acid to undergo hydrogenation in isomerizations in the absence of solvent and catalyst preactivation under hydrogen [15].

5. Conclusions

Double bond migration of linoleic acid to *cis*-9,*trans*-11-conjugated linoleic acid and *trans*-10,*cis*-12-conjugated linoleic acid on H_2-preactivated as well as non-preactivated Ru/Al_2O_3 catalyst was studied at 135–165 °C under kinetic control in a slurry reactor under atmospheric pressure in *n*-decane solution in order to develop a mechanistic model based on an elementary step reaction network to get information on the role of chemisorbed hydrogen on the isomerization kinetics. The catalyst was characterized by using nitrogen adsorption, X-ray photoelectron spectroscopy, scanning electron microscopy–energy dispersive X-ray analysis, and temperature programmed desorption of hydrogen techniques. Over such catalyst and at the conditions used, the reaction scheme involves competitive isomerization of linoleic acid to CLA isomers as well as hydrogenation of linoleic acid to oleic acid. These competing steps are through a complex relationship strongly affected by chemisorbed hydrogen on the Ru surface. The isomerization rate was enhanced by catalyst preactivation under hydrogen, but increased hydrogen coverage on the Ru surface also restrained the isomerization selectivity.

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