Heterogeneous Catalytic Production of Conjugated Linoleic Acid

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Abstract:
Kinetic experiments in selective isomerization of technical grade (∼55%) linoleic acid to *cis*-9,*trans*-11-conjugated linoleic acid (B) and *trans*-10,*cis*-12-conjugated linoleic (E) acid isomers were performed batchwise at 165 °C over two series of supported metal catalysts, i.e., hydrogen preactivated and nonpreactivated. Activated carbon- and aluminium oxide-supported Ru, Pd, Os, Ir, and Pt−Rh catalysts with 5 wt % metal loading were screened. Catalyst characterization was done by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy−energy-dispersive X-ray analysis (SEM−EDX), temperature-programmed desorption of hydrogen (H₂-TPD), direct current plasma atomic emission spectrometry (DCP-AES), and nitrogen adsorption techniques. Over such catalysts, the reaction scheme 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. Over Ru/C catalyst, chemisorbed hydrogen on the metal surface dramatically *increased* the linoleic acid isomerization rate in a diluted system as an astoichiometric component-enhancing double bond migration but *decreased* the isomerization rate by promoting deactivation in a solvent-free system. Over Ru/Al₂O₃ catalyst, on the other hand, dissociated hydrogen increased the isomerization rate for both the diluted and nondiluted systems. The effect of eliminating the solvent was an increase of the turnover frequency (TOF) at 165 °C by a factor of 12 with respect to that shown in a diluted system. At the same conversion carbon- and aluminium oxide-supported Ru catalyst showed higher selectivity toward B and E than carbon-supported Pd, Os, Ir, and Pt−Rh catalysts.

1. Introduction

Conjugated linoleic acid (CLA), which was identified as late as 1987, is being sold as a panacea that has the capability of reducing or even eliminating atherosclerosis and cancer, preventing heart disease, improving immune function, increasing insulin sensitivity, and altering the body composition in order to treat obesity or build lean body mass. Much attention has been paid to the physiological effects of CLA on animals and humans for the past decade; the term *functional food* is increasingly used as a generic description for the beneficial effects of ingested foods that go beyond their traditional nutritive value and CLA is of huge interest for food and health research due to its anticarcinogenic and antioxidative properties .[1−9]

CLA (naturally present in meat and dairy products, where it is synthesized from linoleic acid by rumen bacteria) is a collective term for describing the positional and geometric conjugated dienoic isomers of linoleic acid (*cis*-9,*cis*-12-octadecadienoic acid). Linoleic acid (the main constituent of vegetable oils) 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. Recent findings suggest that not only is CLA effective in many different pathways, but that individual isomers of CLA act differently. Positive health benefits are ascribed to the consumption of the *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers. The dietary significance of the other isomers is unknown.

It has recently been concluded[10] that CLA can be prepared by isomerization of linoleic acid over heterogeneous supported metal catalysts, which due to the cleaner chemistry

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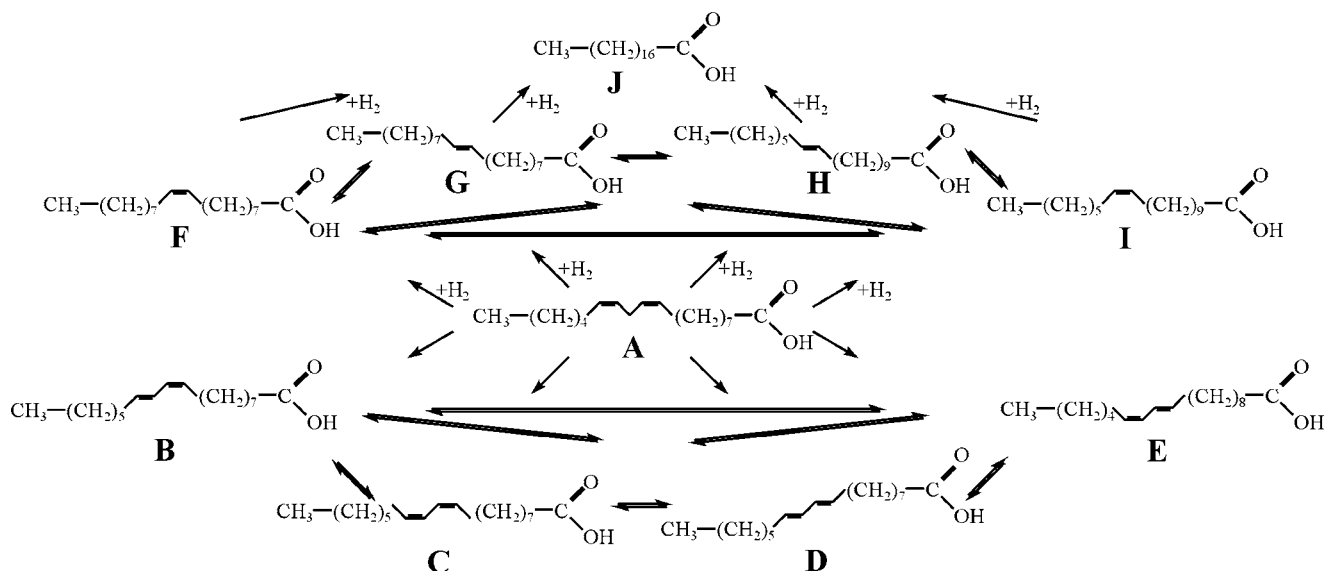
Figure 1. Main reaction network in isomerization and hydrogenation of linoleic acid over supported metal catalysts. (A) linoleic acid; (B) *cis*-9,*trans*-11-conjugated linoleic acid; (C) *cis*-9,*cis*-11-conjugated linoleic acid; (D) *trans*-9,*trans*-11-conjugated linoleic acid; (E) *trans*-10,*cis*-12-conjugated linoleic acid; (F) oleic acid; (G) elaidic acid; (H) *trans*-vaccenic acid; (I) *cis*-vaccenic acid; (J) stearic acid.

is an attractive alternative to the traditional homogeneously[11] catalyzed linoleic acid isomerizations. A new heterogeneously catalytic pathway has been developed for isomerization of linoleic acid to CLA at mild reaction conditions in a diluted system under a nitrogen atmosphere with hydrogen preadsorbed on the catalyst surface.[12] It was shown that isomerization and hydrogenation of linoleic acid are two competing parallel reactions and that these reactions are influenced by the concentration of chemisorbed hydrogen. The pathway for the isomerization and hydrogenation of linoleic acid is demonstrated in Figure 1. Linoleic acid does not only react to the *cis*-9,*trans*-11-, *trans*-10,*cis*-12-, *cis*-9,*cis*-11-, and *trans*-9,*trans*-11-CLA isomers and monoenoic acids, but also to several other CLA isomers (the *cis,cis, trans,trans, cis,trans,* and *trans,cis* isomers of the 7,9-, 8,10-, 9,11-, 10,12-, and 11,13-C_{18} diene acids). Chemical compounds linoleic acid, *cis*-9,*trans*-11-conjugated linoleic acid, *cis*-9,*cis*-11-conjugated linoleic acid, *trans*-9,*trans*-11-conjugated linoleic acid, *trans*-10,*cis*-12-conjugated linoleic acid, oleic acid, elaidic acid, *trans*-vaccenic acid, *cis*-vaccenic acid, and stearic acid are hereafter in text referred to as **A**, **B**, **C**, **D**, **E**, **F**, **G**, **H**, **I**, and **J**, respectively. Isomerization experiments under hydrogen resulted in hydrogenated end products, and experiments under nitrogen resulted in low catalytic activity; however, the isomerization reaction in a nitrogen atmosphere could be enhanced by catalyst preactivation under hydrogen with remaining high isomerization selectivity.[13]

Moreover, the isomerization properties of several supported metal catalysts have been evaluated with reagent grade (99%) linoleic acid.[14] 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, and 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 metal's 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,[14] exhibit feasible conversion and reasonable selectivity toward functional foods **B** and **E** isomers and, which also is very important, low selectivity toward several undesired conjugated dienoic isomers, especially **D**. 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 aluminium oxide- and carbon-supported Ru catalysts for further studies. Moreover, the isomerization selectivity was optimized by the use of nonpolar solvents such as *n*-nonane and *n*-decane.[15]

In the present contribution comparative experiments in the selective isomerization of technical grade (∼55%) linoleic

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acid to isomers **B** and **E** over aluminium oxide- and carbon-supported metal catalysts are conducted batchwise at mild reaction conditions to evaluate the influence of factors such as reactant purity, presence of solvent, preadsorption of hydrogen on the metal surface, and catalyst deactivation on catalytic activity and isomerization selectivities.

2. Experimental Section

2.1. Materials. Linoleic acid of 99% purity, technical grade linoleic acid of 55% purity (impurities: 35% oleic and 10% palmitic acids), Ru/Al_2O_3, and Ru/C (both with 5 wt % metal loading) were supplied by Fluka (Switzerland). Pd/C catalyst (5 wt %) and the solvent *n*-decane of 95% purity were supplied by Sigma-Aldrich (Germany) and Merck (Germany), respectively. The **B**, **C**, **D**, **E**, and *cis*-11,*trans*-13-CLA isomers of high purity were supplied by Matreya, Inc. (U.S.A.). Synthesis of catalysts Os, Ir, and Pt−Rh on activated carbon was reported in a previous study.[14] The BET specific surface areas and pore size distributions were measured with an automatic physisorption−chemisorption apparatus (Sorptometer 1900, Carlo Erba Instruments), and the pore size distributions were calculated according to the Dollimore−Heal method.

2.2. X-ray Powder Diffraction. X-ray powder diffraction (XRD) measurements on Ru/C were performed using a diffractometer (Philips PW 1800) to determine the Ru crystallite size. The measuring conditions were as follows: generator voltage 50 kV, generator current 40 mA, Cu tube anode, automatic divergence slit, irradiated sample length 12 mm, receiving slit 0.2 mm, step size 0.025°, counting time 5.0 s per step.

2.3. X-ray Photoelectron Spectroscopy. Analysis by X-ray photoelectron spectroscopy (XPS) on Ru/Al_2O_3 was utilized to analyze the chemical composition of the "working" catalyst surface. Before performing XPS, a catalyst sample was preactivated ex situ at 100 °C for 1 h including heating time under a H_2 flow of 100 mL/min in the test reactor to obtain 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 to avoid exposure to air. The measurements were carried out with a Perkin-Elmer PHI 5400 ESCA system equipped with PE software. A detailed description of the XPS measurements were reported in a previous paper.[12]

2.4. Scanning Electron Microscopy. Chemical composition as well as metal particle size of Ru/Al_2O_3 was analyzed by scanning electron microscopy−energy-dispersive X-ray analysis (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°.

2.5. Temperature-Programmed Desorption of Hydrogen. Hydrogen adsorption capacities of Ru/Al_2O_3 and Ru/C were investigated by temperature-programmed desorption of hydrogen (H_2-TPD) using a volumetric flow apparatus (Autochem 2910, Micrometrics) with nitrogen−argon (N_2 99.5%, Ar 0.5%, AGA) as a carrier gas. The Ru catalysts were heated in situ to 100 °C (since 100 °C was used as

H_2-preactivation temperature in the isomerization experiments) with a heating rate of 10 °C/min under a 50 mL/min 100% H_2 flow (AGA), kept at 100 °C for 1 h, cooled to 40 °C with a rate of 3 °C/min under flowing H_2, and flushed with 50 mL/min N_2/Ar for 45 min. The H_2 desorption heating rate was 10 °C/min from 40 to 650 °C, and the catalysts were kept at 650 °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 H_2 signal.

2.6. Isomerization Experiments. The isomerization experiments were conducted in a 200-mL stirred batch reactor, which was provided with a reflux condenser system and a heating jacket. Silicone oil served as a heat-transfer fluid, and the reactor was operating at atmospheric pressure. A measured amount of catalyst was charged into the reactor and preactivated in situ at 100 °C for 1 h including heating time under a H_2 flow of 100 mL/min, because catalyst preactivation under hydrogen dramatically enhances the isomerization rate.[10,12−15] Catalyst preactivation under a N_2 atmosphere was also tested for the sake of comparison. After the preactivation, a 100 mL/min N_2 flow was fed through the reactor for 20 min to achieve an inert atmosphere while heating the system to the reaction temperature 165 °C. The reactant solution comprising (i) 0.2 g of technical grade linoleic acid and 70 mL of the solvent *n*-decane or (ii) 70 mL of technical grade linoleic acid was de-oxygenized by a N_2 flow of the same flow rate and 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 100 mL/min N_2 flow was fed through the reactor during the isomerizations to have an inert atmosphere, and the reactor outlet was locked by a fluid to prevent back-diffusion of oxygen into the mixture. The course of the reaction was followed by withdrawing 1 mL samples from the mixture periodically through a 7-μm catalyst filter to await analysis by gas chromatography. The temperature of the cooling medium for the reflux condensers was set to −20 °C, and stirring baffles were used inside the reactor.

The system was typically stirred at 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 overall reaction rates from isomerizations of both reagent and technical grade linoleic acid at varied stirring rates and catalyst quantities but otherwise using the same reaction conditions.

Deactivation of the 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 by pouring or stirring in a tank, dried overnight at 100 °C, and rereduced at 400 °C for 4 h under 100 mL/min flowing 100% H_2 (AGA).

2.7. Analysis. 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 chro-

Table 1. Pore size distribution of the aluminium oxide- and carbon-supported Ru (5 wt %) catalysts

pore ranges (nm)	relative volume (%)	
	5 wt % Ru/Al$_2$O$_3$	5 wt % Ru/C
0−0.9	0	0
0.9−1.0	0	2.6
1.0−1.5	0	5.9
1.5−2.0	0	4.2
2.0−5.0	3.2	20.8
5.0−10.0	25.0	18.1
10.0−100.0	50.6	48.4

matograph (GC, Hewlett-Packard 6890 Series) equipped with a 25-m HP-5 column (inner diameter: 0.20 mm, 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 one isomerization reaction in parallel. A detailed description of the silylation procedure is given in previous reports.[12,14,15] Identities of peaks were verified by a gas chromatograph/mass spectrometer system (GC/MS, Hewlett-Packard) applying the same GC conditions.

3. Results & Discussion

3.1. Catalyst Characterization. *3.1.1. Physio−Chemical Properties of Supported Ruthenium Catalysts.* The BET specific surface areas of the Ru/C and Ru/Al$_2$O$_3$ (5 wt %) catalysts were determined to be 841 and 156 m^2/g, respectively. All catalyst powders consisted of particles smaller than 180 μm. The catalyst particle sizes of Ru/Al$_2$O$_3$ were within the range 0−63 μm. The particle sizes of Ru/C were distributed around 90 μm, with the finest particles less than 45 μm. The pore size distribution of Ru/Al$_2$O$_3$ and Ru/C is given in Table 1. The supports are porous materials with majority of the pore sizes in the range 10−100 nm. Ru/C also has a small relative pore volume fraction less than 2 nm.

The average Ru crystallite size of the Ru/C catalyst was determined to be 50 nm, as measured by XRD, indicating that most of the Ru crystallites are located on the outside of the micropores of the carbon support. The Ru/Al$_2$O$_3$ catalyst had a rather wide metal particle size distribution. In the scanning electron micrographs of Ru/Al$_2$O$_3$ that are presented in Figure 2, it is clearly visible that the average Ru crystallite size is close to that of Ru/C, but some larger agglomerates were found. The electron diffraction indicated a chemical compositions of 27.7 atom % 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, 6.19 wt %. The ratio between the chemical composition of elements Al and O analyzed by XPS is identical to that analyzed by SEM−EDX, while XPS results show only 0.5 atom % of Ru. Moreover, as analyzed by XPS, the Ru/Al$_2$O$_3$ sample included a large amount of C, probably because of contamination. The metallic state of Ru dominates, but the Ru 3d$_{5/2}$ spectra of the samples indicated that Ru species is not only metallic, but a part of Ru may also contain some higher oxidation states which was indicated by a slight broadening of the spectrum to higher binding energy side.

3.1.2. Hydrogen-Adsorption Capacity of Ruthenium. The H$_2$-TPD patterns of Al$_2$O$_3$- and C-supported Ru are demonstrated in Figure 3. Ru/C had 2.3 times higher H$_2$-adsorption capacity than Ru/Al$_2$O$_3$, and the TPD measurements indicated presence of some spillover H$_2$ on Ru/Al$_2$O$_3$. For both catalysts, as much as 90% of the total amount of chemisorbed H$_2$ remained on the metal surface after a temperature increase to 100 °C, which was used as preactivation temperature in the isomerization experiments, and both catalysts exhibited a maximum H$_2$ desorption rate at 125 °C. For Ru/Al$_2$O$_3$, 49% of the total amount of chemisorbed H$_2$ remained on the catalyst surface after a temperature increase to 165 °C, which was used as reaction temperature in the isomerization experiments. The corresponding value for Ru/C was 55%.

3.2. External and Internal Diffusion. To eliminate effects of external transport of linoleic acid to the outer surface of the catalyst particles on reaction rates and to keep the catalyst uniformly dispersed in the reaction medium, the system was agitated at 800 rpm in all experiments. To confirm the negligibility of resistance on the isomerization rate by external transport, the reaction was conducted at 165 °C with varied stirring rates and catalyst quantities but otherwise using the same reaction conditions for both the systems: (a) *n*-decane diluted reagent grade linoleic acid catalyzed by Ru/Al$_2$O$_3$ and (b) solvent-free technical grade linoleic acid catalyzed by Ru/C. It was visually confirmed that the catalyst particles were lifted from the bottom of the glass reactor at the stirring rate 500 rpm and no changes in the dark color of the reaction medium were noted with further increase of the agitation. These observations were consistent with the obtained reaction rate data (Figure 4). No selectivity changes were observed when the stirring rate was varied. It can thus be concluded that external diffusion did not affect catalytic activity or selectivity.

Experiments with catalysts of varied particle size demonstrated that with particle diameter decrease, the initial rate was first inversely proportional to the particle size and thereafter approached a constant value and a plateau of initial rate against particle diameter dependence. It was concluded that for Ru/C[15] the chemical regime[16] with an effectiveness factor larger than 0.95, could be attained at the particle diameter 25 μm, while the aluminium oxide-supported ruthenium catalyst with particle diameters less than 63 μm showed negligible internal diffusion.

3.3. From Reagent Grade Raw Material to Technical Grade. *3.3.1. Diluted System. 3.3.1.1. Catalytic Activity.* For the sake of comparison, technical grade linoleic acid was tested as a raw material instead of previously reported[10,12−15] reagent grade linoleic acid; otherwise identical reaction conditions were used. Polymerization, cracking, or skeletal isomerizations of fatty acids were not observed. No other reactions were detected except for the following 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 hydroge-

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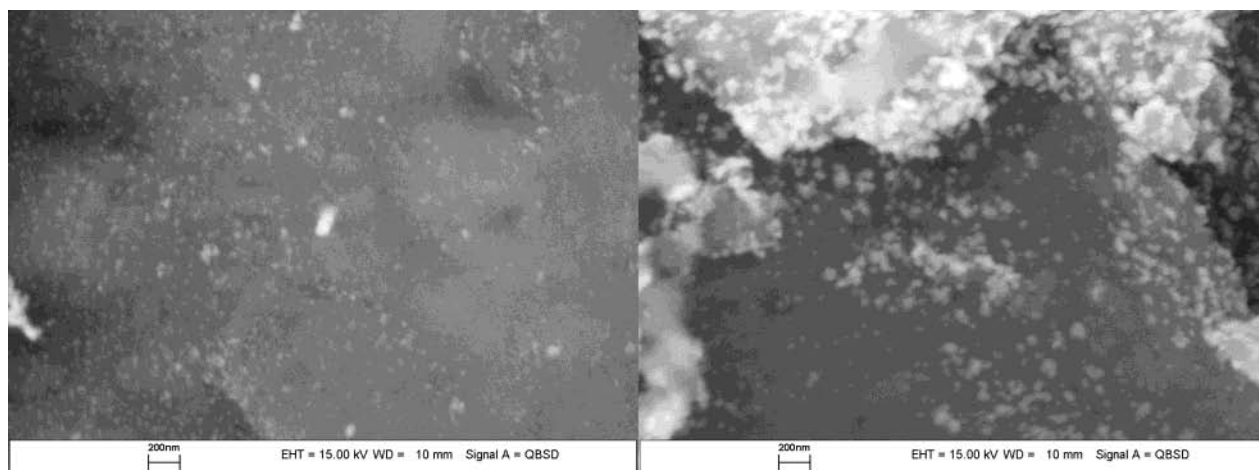
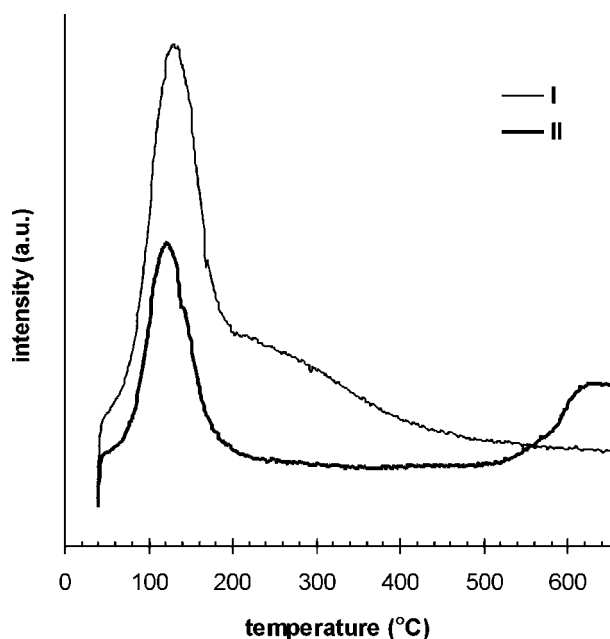**Figure 2.** Scanning electron micrographs of Ru/Al$_2$O$_3$, ×30000.

Figure 3. Hydrogen temperature-programmed desorption patterns of 5 wt % loaded (I) activated carbon- and (II) aluminium oxide-supported ruthenium catalysts.

nation 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. Hence, 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.

The total conversion of linoleic acid after 3 h, the isomerization selectivity at 30% conversion, the selectivity toward **B** and **E** CLA isomers (desired products) at 30% conversion, and the turnover frequency (TOF) after 3 h (based on mol of converted linoleic acid after 3 h/(mol of Ru × 3 h)) kept approximately the same values of 49%, 72%, 25%, and 3.49 × 10^{-4} s^{-1}, correspondingly, and the initial rate (based on total linoleic acid conversion after 30 min and ruthenium mass) increased with a factor of 2, as reagent grade linoleic acid was changed to technical grade. The concentration versus time dependencies are presented

in Figure 5. 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. As demonstrated in Figure 5, the concentration of reagent grade linoleic acid decreases more slowly and continuously with time than the concentration of technical grade linoleic acid, which decreases more rapidly in the beginning of the reaction and thereafter approaches a constant value after a reaction time of 30 min. In both cases the desired **B** and **E** CLA isomers were the main reaction products. In fact, the most thermodynamically stable form is the **D** CLA isomer, which was concluded in isomerization experiments with reagent grade linoleic acid, **B**, **D**, and **E** isomers as reactants over hydrogen preactivated Ru/Al$_2$O$_3$ and Ru/C samples.[16] Several positional and geometric conjugated dienoic isomers are formed as intermediates in the consecutive isomerization of linoleic acid to *trans*-9,*trans*-11-CLA due to the geometry of linoleic acid, the *cis*-9,*cis*-12 form. When CLA isomers were used as reactants, the equilibrium sample did not contain any trace of linoleic acid. When technical grade linoleic acid was used as a raw material, the consumption rate of linoleic acid decreased to zero after a certain period of time. However, the higher initial consumption rate of technical grade linoleic acid in a diluted system is a promising indication in the prospect of a solvent elimination.

3.3.1.2. Overall Isomerization Selectivity. When isomerization is carried out over H$_2$-preactivated Ru catalysts, the isomerization selectivity increases while the hydrogenation selectivity decreases with conversion, since the initially rich layer of chemisorbed hydrogen on the ruthenium surface is consumed in hydrogenation steps during the course of the reaction, indicating that the coverage of hydrogen on the metal surface affects the isomerization and hydrogenation rates. In the beginning of the reaction when the hydrogen coverage on the Ru surface is high, the linoleic acid hydrogenation consecutively proceeding via monoenoic acids to stearic acid is preferred. When, on the other hand, the concentration of chemisorbed hydrogen is low (after some conversion when a majority of the preadsorbed hydrogen has been consumed), isomerization is preferred over hydrogenation.
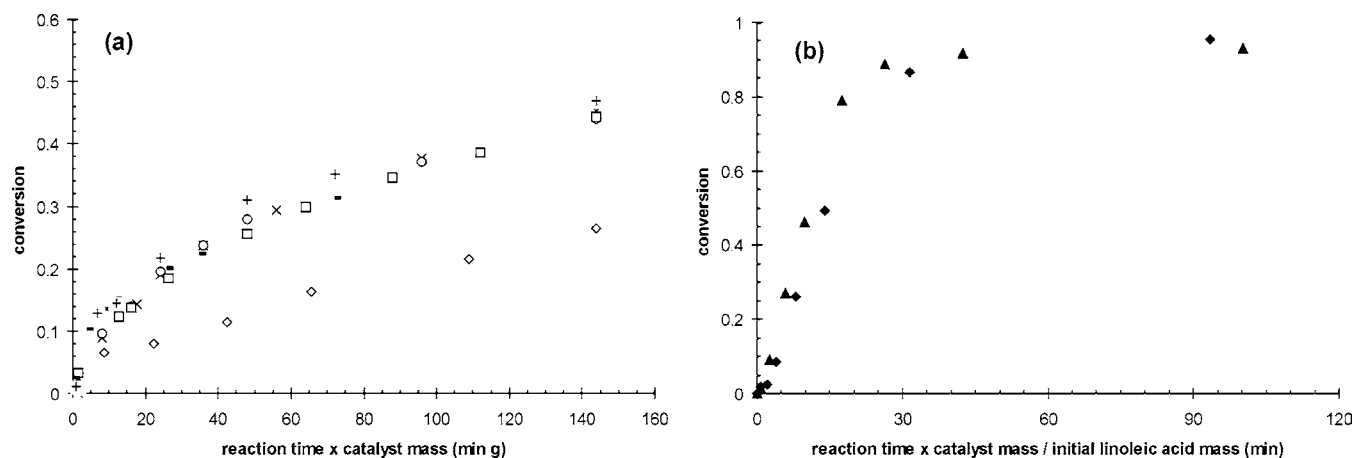
Figure 4. Conversion versus time dependence at varied agitation rate and catalyst quantity for (a) *n*-decane diluted reagent grade linoleic acid catalyzed by Ru/Al$_2$O$_3$ and (b) solvent-free technical grade linoleic acid catalyzed by Ru/C. $\triangle$ = 0/0.8, $\diamondsuit$ = 200/0.8, $\square$ = 500/0.8, $\times$ = 800/0.8, $\bigcirc$ = 1600/0.8, + = 800/0.4, − = 800/0.2 $\blacklozenge$ = 800/3, $\blacktriangle$ = 1600/3 rpm/g.
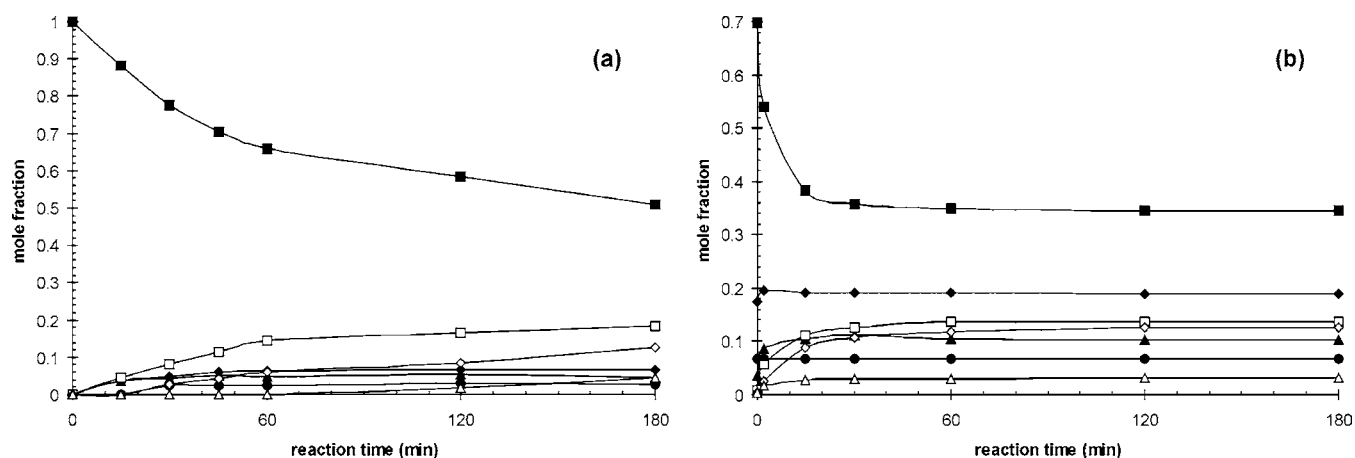

Figure 5. Isomerization of (a) reagent grade and (b) technical grade linoleic acid over H$_2$-preactivated Ru/C in a diluted system. $\blacksquare$ = A; $\blacklozenge$ = F; $\blacktriangle$ = G, H, and I; $\bullet$ = J; $\square$ = B and E; $\diamondsuit$ = D; $\triangle$ = C and other CLA isomers. Conditions: raw material, 200 mg of linoleic acid; reaction temperature, 165 °C; solvent, 70 mL of *n*-decane; stirring rate, 800 rpm; catalyst mass, 200 mg; metal loading, 5 wt %; preactivation temperature, 100 °C; preactivation time, 1 h; reaction pressure, 1 atm of nitrogen.

3.3.1.3. Temperature Effects. The reaction temperature affects activity and selectivity by adjusting the coverage of dissociated hydrogen on the ruthenium metal surface. An increase of the reaction temperature results in a decrease of the catalytic activity and an increase of the isomerization selectivity. The influence of the reaction temperature on reaction rate and selectivities in isomerization of reagent grade linoleic acid over Ru/C and Ru/Al$_2$O$_3$ catalysts was reported in our previous study.[15] When the isomerization was conducted over hydrogen-preactivated Ru/C (5 wt %, 200 mg) using *n*-decane as a solvent, 3 h conversion and initial rate (based on total converted amount of linoleic acid after 30 min and total catalyst mass) decreased from 72% and 4.06 × 10^{-7} mol s^{-1} g^{-1} to 49% and 2.18 × 10^{-7} mol s^{-1} g^{-1}, respectively, as the reaction temperature was elevated from 120 to 165 °C. Moreover, the isomerization selectivity increased from 66 to 85%, and the selectivity toward the desired conjugated linoleic acid isomers increased from 24 to 37%. The reason for decreased rate and conversion and increased isomerization selectivity is the lower amount of chemisorbed hydrogen on the surface of the ruthenium metal. It appears that the double bond migration is no longer

diminished by hydrogenation at this temperature level, that is 40 °C higher than the temperature corresponding to the maximum hydrogen desorption rate indicated by the H$_2$-TPD measurements on Ru/C as demonstrated in Figure 3. Therefore 165 °C was selected as a reaction temperature for further studies.

Ru/C is a more active catalyst than Ru/Al$_2$O$_3$ in isomerization of linoleic acid. Experiments at 120 °C reaction temperature in *n*-decane over Ru/Al$_2$O$_3$ (5 wt %, 200 mg) previously preactivated at 100 °C under hydrogen resulted in 44% conversion at a reaction time of 6 h, 65% overall isomerization selectivity, and 28% selectivity toward **B** and **E**.[15] However, similarly as for the Ru/C catalyst, conversion and initial rate decreased from 44% and 3.27 × 10^{-7} mol s^{-1} g^{-1} to 31% and 1.29 × 10^{-7} mol s^{-1} g^{-1}, respectively, as the reaction temperature was elevated from 120 to 165 °C, and the overall isomerization selectivity increased from 65 to 89%, due to the lower amount of chemisorbed hydrogen. The selectivity toward the desired products **B** and **E** increased from 28 to 58%. Here, the 3 h TOF was 1.53 × 10^{-4} s^{-1}. At similar conditions, the corresponding value for Ru/C was 3.27 × 10^{-4} s^{-1}.

Additional experiments were conducted (at the conditions above) over 800 mg of hydrogen-preactivated Ru/Al$_2$O$_3$ samples in *n*-decane 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 on the Ru surface of chemisorbed hydrogen, which in turn is strongly influenced by the temperature. Initial rate and TOF after 3 h were first slightly increasing with temperature. As the reaction temperature was elevated from 135 °C via 145 °C to 155 °C, the TOF increased from 0.38×10^{-4} s^{-1} via 0.43×10^{-4} s^{-1} to 0.83×10^{-4} s^{-1}, correspondingly, and stayed at this level after a further increase of the temperature to 165 °C. 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 lower temperature limit for an optimization of rate and selectivity by manipulating the hydrogen coverage of the metal surface. The overall isomerization selectivity and the selectivity toward desired products increased with conversion.

3.3.1.4. Catalyst Deactivation. As demonstrated in Figure 4a, the conversion versus time and catalyst mass dependence in reagent grade linoleic acid isomerization falls on the same curve for three different quantities of Ru/Al$_2$O$_3$, which indicates that not only is the reaction conducted in the absence of external diffusion but also that the extent of the catalyst being subject to a reduction in activity with time is either the same independent catalyst mass or negligible. At the same time, the selective Ru/Al$_2$O$_3$ catalyst showed lower activity in a second consecutive experiment over the same catalyst sample that in the regeneration step had been separated from the fatty acid solution by vacuum filtration, washed with acetone in an agitated tank, dried overnight, and rereduced under flowing H$_2$ using the conditions described in the Experimental Section. In the second run, the isomerization selectivity at 30% conversion remained at approximately 90%, and with respect to conversion, initial rate, and TOF, the activity decreased by a factor of more than 2.3. The BET specific surface area kept a constant value of 156 m^2/g as the Ru/Al$_2$O$_3$ catalyst was being used and regenerated twice, and the pore volume distribution presented in Table 1 was not affected; hence, the reason for the observed deactivation could lie within fouling on the active ruthenium sites or poisoning rather than irreversible plugging of pores by the heavy fatty acid molecules. In general, acidic supports or catalysts are especially prone to coking, whereas very little coke forms on activated carbon supports.[15] While consecutively repeating isomerizations and regenerations on the same Ru/C catalyst sample no significant loss in activity was observed, and the BET area decreased only slightly from 840 to 749 m^2/g after five uses. Hence, it appears that the observed deactivation is not due to blocking of the pores of the activated carbon and aluminium oxide support materials by fatty acid compounds. Identical pore volume distributions for carbon- as well as aluminium oxide-supported ruthenium were obtained from nitrogen adsorption measurements on fresh and used catalysts.

3.3.2. Reaction Mechanism. Speaking in terms of molecular mechanisms, the double bond migration reaction of linoleic acid to CLA over supported metal catalysts takes place through several routes besides the main pathway over metal sites. Acid-catalyzed isomerization may also occur over oxidic metal sites. Moreover, if the first step 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. 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 a different carbon atom results in double bond migration.[17]

The observed[10,12−15] enhancement of TOF and initial rate by H$_2$ preactivation of the ruthenium catalysts can be explained by the Horiuti−Polanyi mechanism[18] describing hydrogenation and isomerization of olefins. After the initial H$_2$ preactivation, linoleic acid is chemisorbed on the Ru 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, hydrogen abstraction by the metal takes place from an adjacent carbon atom, which could lead to a double bond migration, depending on which carbon atom the hydrogen is abstracted from. If, on the other hand, the coverage of hydrogen is high, a second hydrogen atom is 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 results in *cis*/*trans*-isomerizations. The role of the Horiuti−Polanyi mechanism in isomerization of butenes was investigated already in 1974[19] by studying the deuterium distribution of exchanged and isomerized olefins obtained from *cis*-butene, *trans*-butene, and but-1-ene on iron films in the presence of perdeuteriopropene. As it is in line with our results, the Horiuti−Polanyi mechanism is valid independent of the length of the carbon chain of the olefin molecule.

3.3.3. Nondiluted System. 3.3.3.1. H$_2$-Preactivated Metal Catalysts. Table 2 summarizes activity and selectivity data on nonpreactivated and H$_2$-preactivated aluminium oxide- and carbon-supported 5 wt % ruthenium, palladium, osmium, iridium, and bimetallic platinum−rhodium catalysts in isomerization of nondiluted technical grade linoleic acid. The effect of eliminating the solvent was to increase the TOF at 3 h by a factor of 12 compared to that shown in an *n*-decane diluted system. This increase of the TOF is not only caused by the observed solvent effect but also by the use a drastically higher reactant-to-catalyst mass ratio, which in turn contributes to an increased TOF.

(17) Ramani, N. C.; Sullivan, D. L.; Ekerdt, J. G. Isomerization of 1-Butene over Silica-Supported Mo(VI), W(VI), and Cr(VI). *J. Catal.* **1998**, *173*, 105−114.
(18) Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversions*; Academic Press: New York, 1981.
(19) Touroude, R.; Gault, F. G. The Mechanism of Isomerization and Exchange of Olefins Over Metal Catalysts. *J. Catal.* **1974**, *32*, 294−303.

Table 2. Activity and selectivity data on ruthenium, palladium, osmium, iridium, and platinum−rhodium catalysts supported by aluminium oxide and activated carbon in technical grade linoleic acid isomerization[a]

no.	catalyst	catalyst preactivation	linoleic acid mass/catalyst mass	conv.[b]	S_I[c]	S_D[d]	initial overall reaction rate[e] (10^{-5} mol s^{-1} g^{-1})	TOF[f] (10^{-4} s^{-1})	BET area before use (m^2/g)	BET area after use (m^2/g)
1	Ru/C	yes	14.1	0.72	0.98	0.63	2.70	8.46	841	604[g]
2	Ru/C	yes	16.8	0.50	0.97	0.67	2.21	6.99	841	−
3	Ru/C, 2nd run[g]	yes	18.1	0.23	0.94	0.58	0.89	3.46	604[g]	700[g]
4	Ru/Al$_2$O$_3$	yes	15.0	0.81	0.95	0.59	2.32	10.12	156	167[g]
5	Ru/Al$_2$O$_3$, 2nd run[g]	yes	18.3	0.08	−	−	0.48	1.22	167[g]	147[g]
6	Ru/C	no	15.0	0.95	0.98	0.56	3.61	11.87	841	767[g]
7	Ru/C	no	17.1	0.85	0.96	0.56	2.99	12.12	841	−
8	Ru/C, 2nd run[g]	no	17.8	0.68	0.76	0.45	3.00	10.11	767[g]	808[g]
9	Ru/C, 2nd run[h]	no	15.8	0.81	0.93	0.54	2.96	10.64	643[h]	577[h]
10	Ru/C[i]	no	13.7	0.89	0.96	0.61	4.02	10.15	841	643[h]
11	Ru/Al$_2$O$_3$	no	15.2	0.03	−	−	0.10	0.38	156	−
12	Pd/C	no	13.5	0.61	0.68	0.30	1.69	7.22	804	550[h]
13	Os/C	no	13.4	0.24	0.68	0.34	0.49	5.07	610	−
14	Ir/C	no	15.1	0.65	0.46	0.21	2.39	15.55	784	−
15	Pt−Rh/C[j]	no	15.2	0.51	0.66	0.31	1.60	10.84	690	−

[a] Conditions: raw material, 70 mL of technical grade linoleic acid; reaction temperature, 165 °C; stirring rate, 800 rpm; catalyst metal loading, 5 wt %; catalyst particle diameter interval, 0−180 μm; catalyst preactivation temperature, 100 °C; catalyst preactivation time, 1 h; reaction pressure, 1 atm of nitrogen; reaction time, 24 h. [b] Total conversion of linoleic acid (**A**) after 24 h. [c] Selectivity toward isomerization at 30% conversion. S_I = mole fraction of all CLA isomers at 30% conversion /0.3. [d] Selectivity toward desired CLA isomers at 30% conversion. S_D = mole fraction of *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers (**B** and **E**) at 30% conversion/ 0.3. [e] Based on total linoleic acid conversion after 6 h and metal mass. [f] Turnover frequency. TOF = mol of converted linoleic acid after 24 h/(mol of metal × 24 h). [g] Catalyst sample had been filtered, washed by pouring 200 mL of acetone through the filter cake, dried overnight at 100 °C, reduced under a 100 mL/min hydrogen flow at 400 °C for 4 h, and passivated after reaching room temperature by exposure to air. [h] Catalyst sample had been filtered, washed by pouring 200 mL of acetone through the filter cake, additionally washed in 200 mL of acetone at its boiling point (57 °C) in an 800 rpm stirred tank for 2 h, filtered, and washed again by pouring 200 mL of acetone through the filter cake, dried overnight at 100 °C, reduced under a 100 mL/min hydrogen flow at 400 °C for 4 h, and passivated after reaching room temperature by exposure to air. [i] Stirring rate: 1600 rpm. [j] Metal loading: 5 wt % Pt + 0.05 wt % Rh.
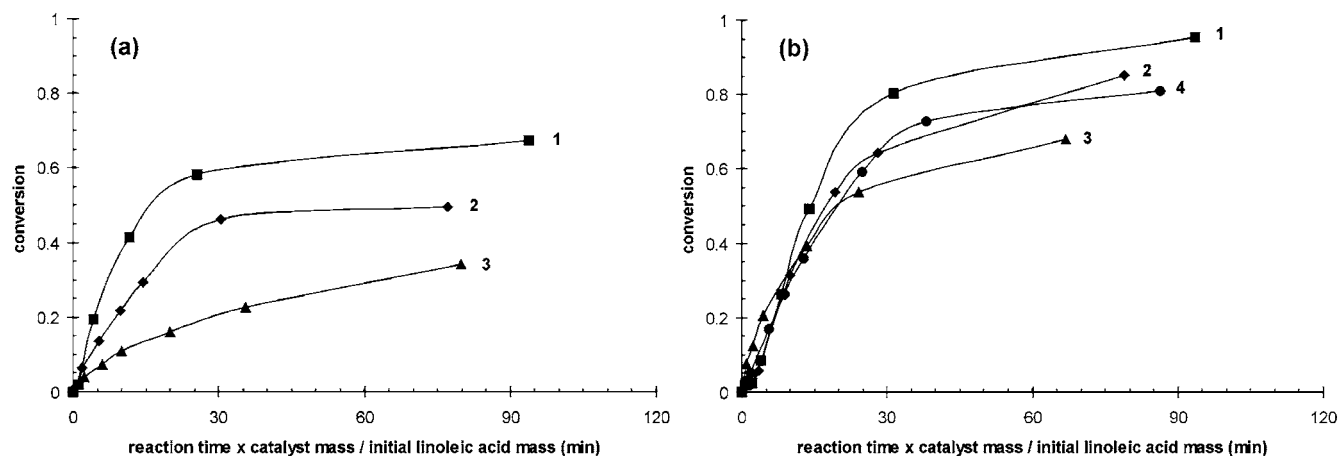

Figure 6. Study of deactivation of (a) H$_2$-preactivated and (b) nonpreactivated Ru/C catalyst in isomerization of technical grade linoleic acid in a solvent-free system. ■ = 3 g of Ru/C, first run; ◆ = 2 g of Ru/C, first run; ▲ = 2 g of Ru/C, second run; ● = 2 g of Ru/C, second run (catalyst was washed under agitation). Conditions: raw material, 70 mL of technical grade linoleic acid; reaction temperature, 165 °C; stirring rate, 800 rpm; metal loading, 5 wt %; preactivation temperature, 100 °C; preactivation time, 1 h; reaction pressure, 1 atm of nitrogen.

In technical grade linoleic acid isomerization in a non-diluted system, an increase of the reactant-to-catalyst mass ratio had a significant effect on the course of the reaction (Table 2, entries 1 and 2) compared to the case of reagent grade linoleic acid isomerization in a diluted system.[12−15] Figure 6 a demonstrates that observed activity depends on catalyst mass, which is an indication of differences in available surface coverage as well as of some catalyst deactivation. In addition, the BET specific surface area decreased from 841 to 604 m^2/g as the Ru/C catalyst was being used and regenerated by filtration, washing, and high-temperature reduction under H$_2$. Selectivities were not affected by the reactant-to-catalyst mass ratio. In the isomerization experiment conducted over fresh H$_2$-preactivated Ru/C catalyst, no significant leaching of the Ru metal by the fatty acids was detected, which indicates that the isomerization and hydrogenation reactions do not occur in the homogeneous phase. The Ru content of the fatty acid
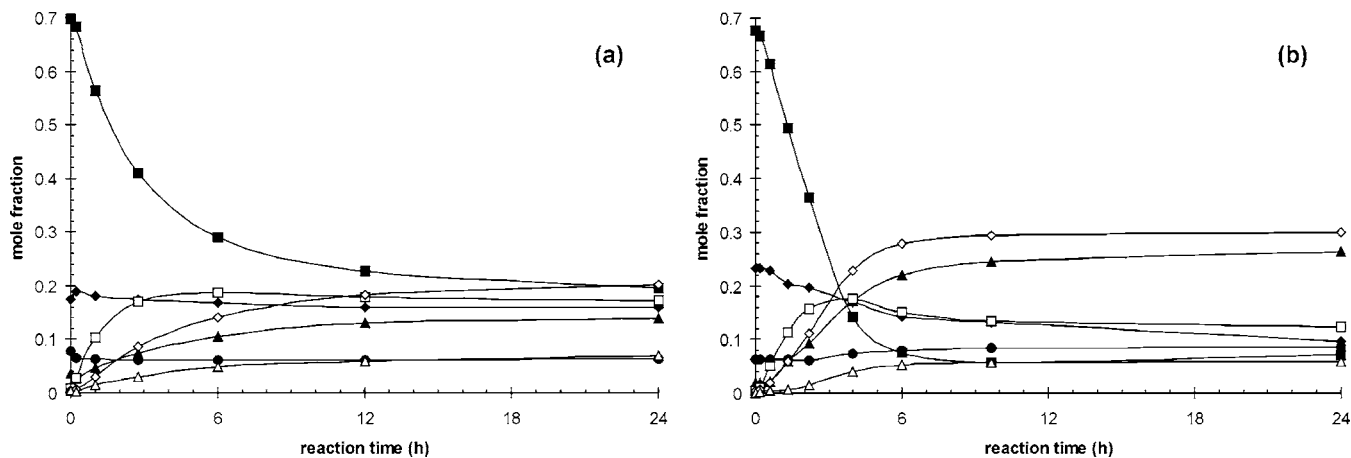
Figure 7. Isomerization of solvent-free technical grade linoleic acid over (a) H_2-preactivated and (b) nonpreactivated Ru/C. ■ = A; ◆ = F; ▲ = G, H, and I; ● = J; □ = B and E; ◇ = D; △ = C and other CLA isomers. Conditions same as Figure 6.

solution after a reaction time of 24 h was 8 μg/mL as determined by direct current plasma atomic emission spectrometry (DCP-AES).[20]

Consecutive experiments with regenerated Ru/C also confirmed nonnegligible deactivation (Figure 6a and Table 2, entries 2 and 3); moreover a lowered value of the BET area after use was obtained (700 m^2/g). The isomerization selectivity and the selectivity toward the **B** and **E** remained at a very high level in the second run over the regenerated catalyst.

The H_2-preactivated Ru/Al$_2$O$_3$ catalyst showed catalytic activity and isomerization selectivity as high as the H_2-preactivated Ru/C catalyst, and the BET area of the support material kept an approximately constant value of 160 m^2/g in the isomerization (Table 2, entry 4). Independent of the support material, the hydrogen-preactivated ruthenium catalysts showed approximately the same selectivity toward double bond migration and the desired conjugated linoleic acid isomers, as well as TOF. However, the Ru/Al$_2$O$_3$ catalyst was not longer active in a second run (Table 2, entry 5), in which the BET area changed only slightly from 167 to 147 m^2/g. Here the initial rate and TOF decreased by a factor of 10.

The reason for the observed deactivation over Ru/Al$_2$O$_3$ could lie within fouling on the active ruthenium sites or poisoning rather than irreversible plugging of pores by the heavy fatty acid molecules since the decrease of BET was minor. Substantial decrease of surface area for Ru/C could be an indication for coking.

3.3.3.2. Nonpreactivated Metal Catalysts. As expected, 24 h conversion, initial rate (based on total linoleic acid conversion after 6 h and metal mass), and TOF (mol of converted linoleic acid after 24 h/(mol of metal × 24 h)) of technical grade linoleic acid over nonpreactivated Ru/Al$_2$O$_3$ were almost negligible (Table 2, entry 11), since no chemisorbed hydrogen on the catalyst surface is available as an astoichiometric compound for promoting double bond migration.

Interestingly, conversion, initial rate, and TOF increased by a factor of more than 30 when nonpreactivated Ru/Al$_2$O$_3$ under identical conditions was changed to nonpreactivated Ru/C (Table 2, entries 11 and 6). The nonpreactivated Ru/C catalyst did also show higher conversion, initial rate, and TOF than the H_2-preactivated Ru/C catalyst (Table 2, entries 1 and 6), at the same time keeping high selectivities, which leaves nonpreactivated Ru/C as the most active and selective catalyst in technical grade linoleic acid isomerization. In addition the surface area remained high for used and regenerated catalyst at 400 °C. The influence of catalyst preactivation under H_2 on the course of the isomerization reaction over Ru/C is illustrated in Figure 7. As seen in Figure 7a, the consumption rate of A over H_2-preactivated Ru/C is close to zero after a reaction time of 12 h. Fatty acid composition at this point, which is not directly related to chemical equilibrium between fatty acids, is through a complex connection influenced by the total amount of chemisorbed hydrogen generated in the catalyst preactivation step, reaction conditions, availability of active vacant sites on the catalyst surface, competitive adsorption between linoleic acid, the solvent, reaction products, and most predominantly by catalyst deactivation. In Figure 7b the dominating consecutive steps, isomerization of linoleic acid via **B** and **E** to **D**, are clearly visible. Initially, the concentration of linoleic acid decreased rapidly according to zero-order kinetics and stayed at a level of 7 mol %. Although oleic acid is the main hydrogenation product of linoleic acid, the concentration of **F** decreased continuously with time, not only due to hydrogenation of **F** to **J** but also due to the geometric isomerization reactions of **F** to **G**, **H**, and **I**, which in turn also contributed to the modest increase of the concentration of stearic acid. The concentrations of **B** and **E** initially increased (as in a typical consecutive reaction) and started to decrease after reaching a maximum value, whereas concentrations of not only **D** but also **C** and other unknown CLA isomers started to build up later than those of the desired isomers. The fatty acid composition at maximum yields of **B** and **E** conjugated linoleic acid isomers is most conveniently demonstrated by the corresponding gas chromatogram (Figure 8).

(20) Ek, P.; Huldén, S. G.; Ivaska, A. Sequential Injection Analysis System for the Determination of Hydride Forming Elements by Direct Current Plasma Atomic Emission Spectrometry. *J. Anal. At. Spectrom.* **1995**, *10*, 121−126.
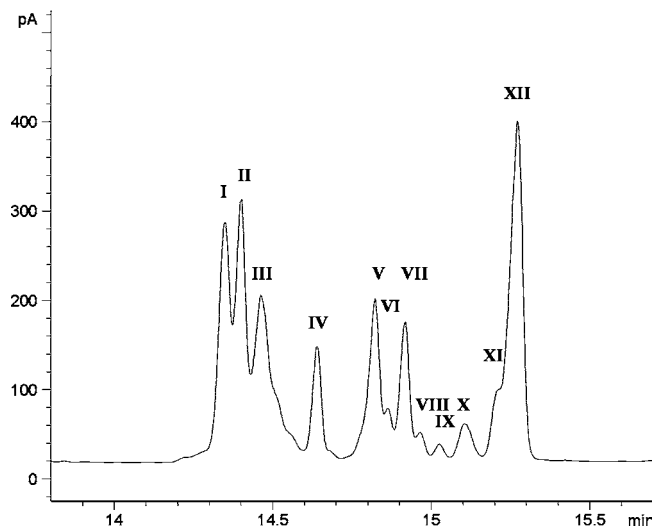
Figure 8. Separation of fatty acids by gas chromatography. I = A; II = F; III = G, H, and I; IV = J; V = B; VI = unknown CLA isomer; VII = E; VIII and IX = unknown CLA isomers; X = C; XI = unknown CLA isomer; XII = D.

In isomerization of technical grade linoleic acid over nonpreactivated Ru/C, a decrease of the catalyst mass from 3 to 2 g (Table 2, entries 6 and 7) indicated some deactivation, similar to the case in isomerization over H2-preactivated Ru/C catalyst. As seen in Figure 6b, the conversion profile decreases slightly when the Ru/C quantity was decreased (curves 1 and 2). As before, selectivities were not affected by the reactant-to-catalyst mass ratio.

In contrast to the case of H$_2$-preactivated Ru/C, identical values of initial rate (6 h) and TOF (24 h) were obtained when the nonpreactivated Ru/C catalyst was regenerated and tested in a second consecutive isomerization experiment over the same catalyst sample. The BET surface area did not change as the catalyst was being used (Table 2, entries 7 and 8), although the conversion after 24 h decreased slightly. In Figure 6b the conversion profiles for the first (curve 2) and the second (curve 3) runs were initially matching but showed a discrepancy at higher conversions.

Two different washing procedures were applied in the catalyst regeneration step to improve the catalyst durability. In the experiment presented in entry 8 (Table 2), the catalyst sample was filtered in the regeneration step, then washed by pouring acetone over the filtrate, dried overnight, and reduced under flowing H$_2$ at 400 °C. In the second regeneration technique, the catalyst was filtered, washed by pouring acetone through the filter cake, stirred in an acetone-filled tank, washed again by acetone pouring, dried overnight, and rereduced. Thus, the main difference in the second procedure was the stirring in acetone. The conditions for both procedures are given in the footnote of Table 2. When a second run over the nonpreactivated Ru/C catalyst was made, it showed catalytic activity and selectivities equal to those of the corresponding isomerization experiment over the fresh catalyst (Table 2, entries 7 and 9). The conversion profiles for both experiments follow the same pattern, as shown in Figure 6b (curves 2 and 4).

In summary, in a solvent-diluted system[15] with low reactant-to-catalyst mass ratio, H$_2$ preactivation of Ru/Al$_2$O$_3$

and Ru/C catalysts followed by isomerization under an inert atmosphere enhanced the isomerization rate compared to that shown in the case of absence of preactivation. H$_2$-preactivated ruthenium metal was more resistant to deactivation when it was supported by carbon than when it was supported by Al$_2$O$_3$. Although, in a nondiluted system with high reactant-to-catalyst mass ratio, H$_2$ preactivation of Ru/Al$_2$O$_3$ similarly enhanced the isomerization rate, contrary to diluted systems, H$_2$-preactivation of Ru/C suppressed the isomerization rate by increasing the catalyst deactivation. The TOF in a nondiluted system with high reactant-to-catalyst mass ratio increased by a factor of more than 30 when nonpreactivated Ru/Al$_2$O$_3$ under identical conditions was changed to nonpreactivated Ru/C. At the present time it can be only speculated that oleic and palmitic acids present in technical grade linoleic acid behave very specifically over H$_2$-preactivated Ru/C, promoting deactivation.

Nonpreactivated palladium, osmium, iridium, and platinum−rhodium catalysts (Table 2, entries 12−15) supported by activated carbon originating from birch wood showed feasible technical grade linoleic acid conversions and turnover frequencies, especially Pd/C, Ir/C, and bimetallic Pt−Rh/C. However, Pd, Os, Ir, and Pt−Rh supported by carbon could not compete with Ru/C with respect to the isomerization selectivity or the selectivity toward **B** and **E**, predominantly due to higher double bond hydrogenation. The fact that the carbon-supported Os, Ir, and Pt−Rh catalysts were synthesized from chlorine-containing precursors might also play a role in the lowered selectivity toward the desired isomers over these catalysts. In addition, the Pd/C catalyst exhibited a higher loss of surface area than the Ru/C catalyst under similar conditions (Table 2, entries 6 and 12). The unique linoleic acid isomerization property of the ruthenium metal is demonstrated in Figure 9. Independent of the support material, the ruthenium catalysts followed the very same selectivity to desired isomers versus conversion, which was higher than the corresponding selectivity pattern of all other investigated metal catalysts. In contrast to isomerizations in a diluted system, where Ru/Al$_2$O$_3$ showed constant selectivities,[15] all catalysts showed a decreasing selectivity to the desired CLA isomers versus conversion dependence in nondiluted technical grade linoleic acid isomerizations; independent of catalyst pretreatment (catalyst preheating under H$_2$ or N$_2$), the selectivity toward overall conjugated linoleic acid and the selectivity toward **B** and **E** decreases with conversion, while the selectivity toward double bond hydrogenation of linoleic acid and the selectivity for **D** increases with conversion.

The mechanism of selective isomerization of linoleic acid into **B** and **E** over metal catalysts supported by activated carbon and aluminium oxide is not fully understood. 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.
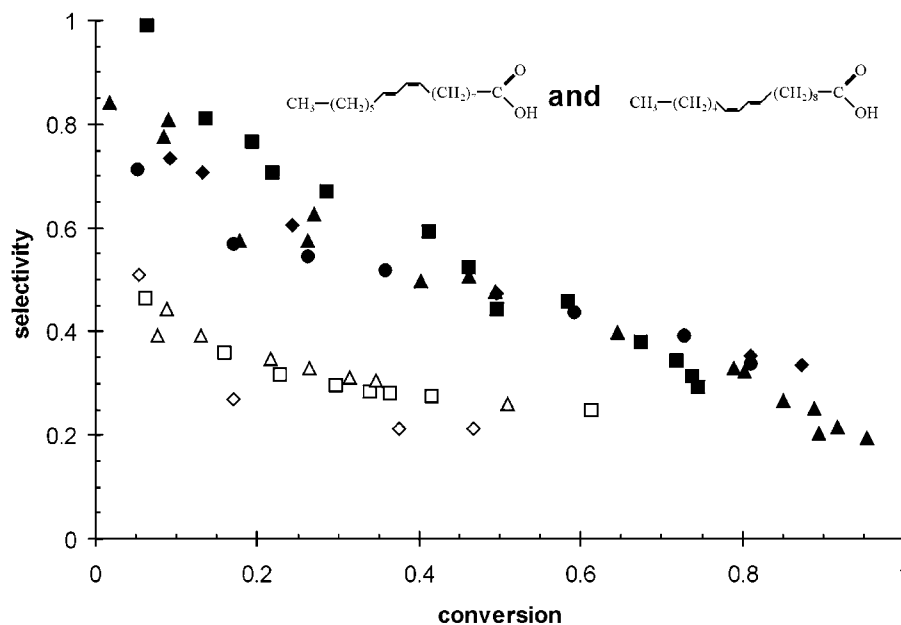
Figure 9. Selectivity toward B and E in isomerization of technical grade linoleic acid over (■) H₂-preactivated Ru/C, (◆) H₂-preactivated Ru/Al₂O₃, (▲) nonpreactivated Ru/C, (●) nonpreactivated Ru/C (second run over regenerated catalyst), and nonpreactivated catalysts (□) Pd/C, (◇) Ir/C, and (△) Pt−Rh/C. Conditions same as Figure 6.

Formation of conjugated linoleic acid isomers is thought to occur via several pathways. Most probably, the dienoic acids are chemisorbed by the diene 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) and desorption of the products. A second possibility, that the acids are chemisorbed via the diene adsorption mode followed by positional or *cis/trans* isomerization of both double bonds and desorption 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 **B** from *cis*-9,*cis*-12-linoleic acid in one step. Similarly, the reaction of *cis*-9,*cis*-12-linoleic acid to **E** 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 **A** decreases and the concentration of **B** form increases, the latter one reacts to the most thermodynamically stable **D** form in a single step by geometric isomerization of the *cis*-9-bond, whereas the *trans*-11-bond is locked. It is clearly seen in Figure 7 that isomerization of **A** to the **D** isomer occurs consecutively in two steps via **B**, 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 diene adsorption mode, positional isomerization of both the double bonds, and desorption, was unmasked as the **E** isomer mainly reacted to the **B**, **C**, and **D** CLA isomers.[15]

A mechanism involving hydride transfer could also be operative. Hydride transfer from the solvent has been discussed in the literature[21] 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.[22] 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.[23] 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.

4. Conclusions

A new and clean process for catalytic isomerization of linoleic acid to biologically active *cis*-9,*trans*-11-conjugated linoleic acid and *trans*-10,*cis*-12-conjugated linoleic acid over solid catalysts has been developed. Experiments were conducted batchwise over carbon- and aluminium oxide-supported Ru, Pd, Os, Ir, and Pt−Rh catalysts using technical grade linoleic acid. Catalyst characterization was done by X-ray powder diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy−energy-dispersive X-ray analysis, temperature-programmed desorption of hydrogen, and nitrogen adsorption techniques. In the present study as well as in some previous publications[10,12−15] the influence of several process parameters such as choice of metal and support material, purity of the raw material, presence of solvent, preadsorption of hydrogen on the metal surface and hydrogen adsorption capacity of the catalyst, linoleic acid and catalyst quantity (i.e. reactant-to-catalyst mass ratio), agitation rate, size of support pores and catalyst particles (i.e., external and internal diffusion), and catalyst deactivation

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on catalytic activity and selectivity was investigated. Migration of the double bond in linoleic acid to yield conjugated linoleic acid occurs simultaneously with positional and geometric isomerization of conjugated linoleic acid, hydrogenation of double bonds in dienoic acids to monoenoic acids, and further to stearic acid as well as positional and geometric isomerization of monoenoic acids. On ruthenium catalysts, the surface coverage of dissociated H_2 and key intermediates have a definite control over catalytic activity and selectivities toward isomerization and hydrogenation products through a complex relationship. A modest H_2 coverage on the metal favors the double bond migration steps, while a high H_2 coverage favors the side reaction i.e. double bond hydrogenation. However, the isomerization rate can be increased by preactivation of the catalyst under a hydrogen atmosphere. By applying a technique of catalyst preactivation, one is balancing on the edge between increased activity and decreased selectivity so that a compromise has to be made to guarantee optimal reaction conditions. The major findings in this contribution can be summarized as follows.

(a) At reaction temperatures higher than 145 °C, chemisorbed hydrogen on the ruthenium surface *increases* the linoleic acid isomerization rate in a solvent-diluted system (with low reactant-to-catalyst mass ratio). Hydrogen acts as an astoichiometric component enhancing metal-catalyzed double bond migration without any major loss of isomerization selectivity due to metal-catalyzed double bond hydrogenation. This effect was observed over catalysts with both carbon and aluminium oxide supports.

(b) In a nondiluted system (with high reactant-to-catalyst mass ratio), chemisorbed hydrogen similarly *increases* the isomerization rate without loss of isomerization selectivity over aluminium oxide-supported ruthenium catalysts, but *decreases* the isomerization rate dramatically by promoting deactivation over carbon-supported ruthenium.

(c) In a solvent-diluted system, H_2-preactivated Ru/C catalyst is very *resistant to deactivation* while H_2-preactivated Ru/Al$_2$O$_3$ undergoes some deactivation. In a nondiluted system, on the other hand, both Ru/C and Ru/Al$_2$O$_3$ catalysts *deactivate considerably* if these catalysts are preactivated under H_2, while nonpreactivated Ru/C catalysts interestingly demonstrate a higher activity with *negligible catalyst deactivation*.

(d) The isomerization rate is higher in a nondiluted system compared to that shown in a solvent-diluted system. This increase of the rate might be caused not only by solvent effects but also by a higher reactant-to-catalyst mass ratio.

(e) Under identical conditions, carbon- and aluminium oxide-supported Ru catalyst showed higher overall isomerization selectivity (at the same conversion) as well as higher selectivity toward the desired *cis*-9,*trans*-11- and *trans*-10,*cis*-12-conjugated linoleic acid isomers (**B** and **E**) than carbon-supported Pd, Os, Ir, and Pt−Rh catalysts.

(f) When isomerization of technical grade linoleic acid is conducted over ruthenium catalysts in a nondiluted system, selectivities are not affected by catalyst deactivation, influence of mass transport, or choice of carbon or aluminium oxide supports.

(g) Independent of catalyst pretreatment (catalyst preheating under H_2 or N_2), the selectivity toward overall conjugated linoleic acid and the selectivity toward *cis*-9,*trans*-11- and *trans*-10,*cis*-12-conjugated linoleic acid (**B** and **E**) decrease with conversion, while the selectivity toward double bond hydrogenation of linoleic acid and the selectivity for *trans*-9,*trans*-11-conjugated linoleic acid (**D**) increase with conversion, when nondiluted technical grade linoleic acid is isomerized over any of the investigated catalysts.