

A New Heterogeneously Catalytic Pathway for Isomerization of Linoleic Acid over Ru/C and Ni/H–MCM-41 Catalysts

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The isomerization reaction of linoleic acid (*cis*-9,*cis*-12-octadecadienoic acid) to conjugated linoleic acids (CLA) was studied. A new heterogeneously catalytic pathway was developed for synthesis of CLA at mild reaction conditions (80–120°C) over Ru/C and Ni/H–MCM-41 catalysts in a diluted system. The isomerization reaction was tested in 1-octanol and *n*-decane. Solvents with low polarity were selected to afford good reactant adsorption on the catalyst surface and a high solvent-to-reactant ratio was used to prevent potential side reactions. Catalyst characterization was done by X-ray powder diffraction, X-ray fluorescence, X-ray photoelectron spectroscopy, hydrogen temperature-programmed desorption, direct current plasma atomic emission spectrometry, and BET techniques. The reactions taking place were isomerization of linoleic acid C_{18:2}, hydrogenation of C_{18:2} acids to C_{18:1} monounsaturated octadecenoic acids (oleic acid, elaidic acid, *cis*-vaccenic acid and *trans*-vaccenic acid), and further hydrogenation of C_{18:1} acids to C_{18:0} stearic acid (*n*-octadecanoic acid) where isomerization and hydrogenation were two competing parallel reactions. The isomerization reaction was enhanced by preactivation of the catalysts under hydrogen, but such a treatment also increased the side reaction double-bond hydrogenation. © 2002 Elsevier Science (USA)

Key Words: functional food; conjugated linoleic acids; Ni/H–MCM-41; double-bond migration; isomerization; hydrogenation.

1. INTRODUCTION

In this paper, a new heterogeneously catalytic pathway is described for the synthesis of conjugated linoleic acids over supported metal catalysts. Conjugated linoleic acids (CLAs), first positively identified in 1987, is a collective term describing the positional and geometric conjugated dienoic isomers of linoleic acid (*cis*-9,*cis*-12-octadecadienoic acid). Linoleic acid (C_{18:2}) 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 (1). Useful analytical data can be obtained through ¹³C NMR of the olefinic carbon atoms. Each CLA isomer has signals for its four olefinic carbon atoms and chemical shifts have been identified for 20 different CLA isomers. These are *cis,cis*; *trans,trans*; *cis,trans*; and *trans,cis* isomers of the 7,9; 8,10; 9,11; 10,12; and 11,13 C₁₈ diene acids. Structures of linoleic acid, monounsaturated octadecenoic acids (oleic acid, elaidic acid, *cis*-vaccenic acid, and *trans*-vaccenic acid), saturated stearic acid (*n*-octadecanoic acid), and CLA isomers are given in Fig. 1.

CLA is naturally present in meat and dairy products. It is found in many animal products, especially those from ruminant sources where it is synthesized from linoleic acid by rumen bacteria (2). The total content of CLA in food varies widely, but the *cis*-9,*trans*-11 isomer has been found to be the predominant form (as much as 80 to 90% of total CLA) (3). Increased dairy fat consumption has been shown to be associated with increased CLA levels in human adipose tissue and human milk (2).

CLA has recently been found to be both anticarcinogenic and antioxidative, hence these fatty acids are of great interest in food and health research. They have been found to affect immunomodulation and body composition alteration, and they can prevent or cure cancer and atherosclerosis (2). Several studies have demonstrated that the *cis*-9,*trans*-11 isomer is responsible for the anticarcinogenic effects of CLA (1, 4). It has also been concluded that the *trans*-10, *cis*-12 isomer produces the changes in body composition that have been observed routinely in mice, rats, and pigs. CLAs have also been linked directly to increased insulin sensitivity, normalized glucose tolerance, improved hyperinsulinemia, and lowered levels of circulating free fatty acids (1).

CLA can be prepared by isomerization of linoleic acid under alkaline conditions. It has been reported that when CLA was synthesized from linoleic acid in a homogeneously catalyzed isomerization reaction, 90% of the product

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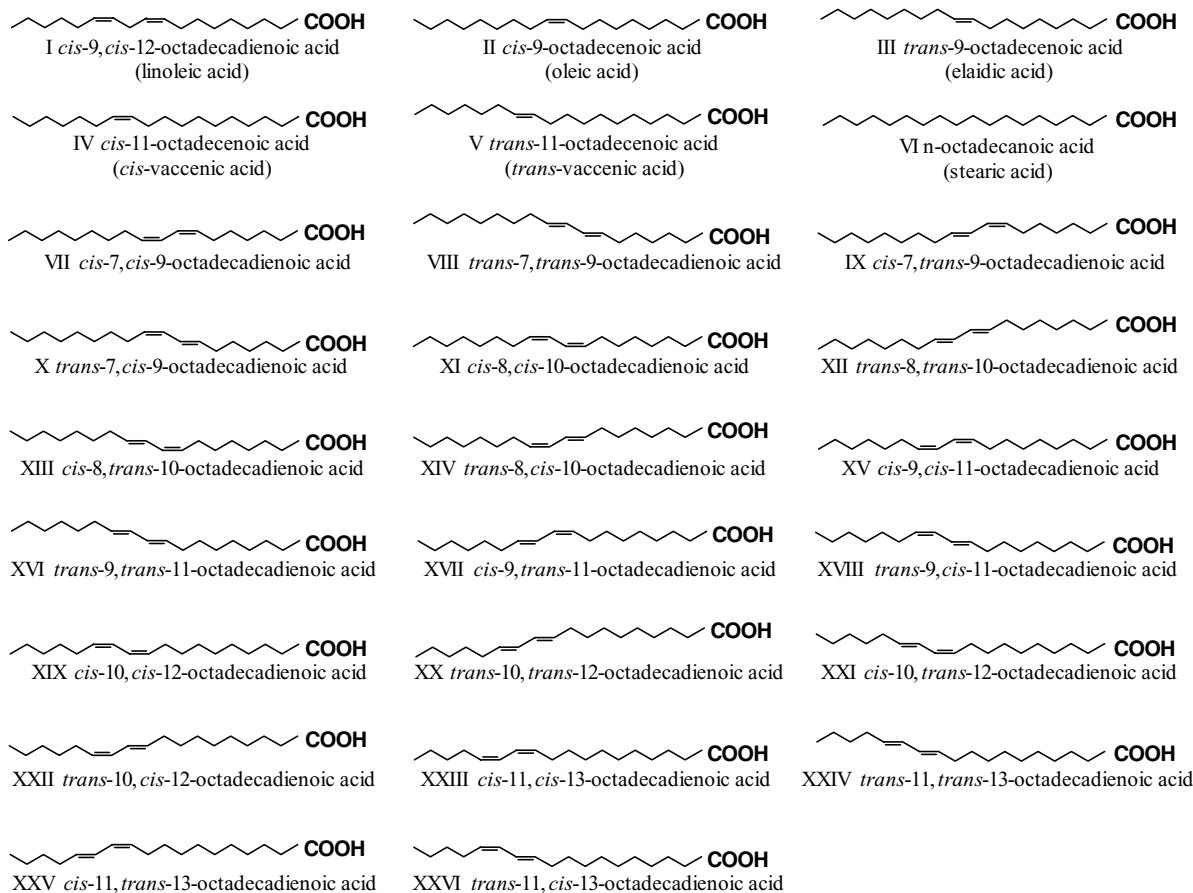


FIG. 1. Structures of linoleic acid ($C_{18}H_{32}O_2$), monounsaturated acids ($C_{18}H_{34}O_2$), saturated stearic acid ($C_{18}H_{36}O_2$), and CLA isomers ($C_{18}H_{32}O_2$).

composition consisted of *cis-9,trans-11*, *trans-10,cis-12*, *trans-9,trans-11*, and *trans-10,trans-12* isomers, and the remaining 10% of *cis-9,cis-11*, *trans-9,cis-11*, *cis-10,cis-12*, and *cis-10,trans-12* isomers, including a minor fraction of the *cis-11,cis-13* isomer (1). In the conventional alkaline isomerization methods for producing conjugated fatty acids, ethylene glycol, dimethyl sulfoxide, or dimethylformamide are used as a solvent (5). When the end product is used in the food industry, the choice of the solvent is limited to the ones that are harmless to the human body. The main disadvantage of alkali isomerization of linoleic acid is the use of excess of strong basic potassium hydroxide or sodium methoxide. Homogeneous catalysts are tris(triphenylphosphine)chlororhodium (6) and arene chromiumcarbonyl complexes (7), which are difficult to reuse and not environmentally friendly.

Instead, a heterogeneous catalyst would be easy to filter and reuse. Several possibilities exist to isomerize methyl linoleate, the ester of linoleic acid, over heterogeneous catalysts. Isomerization reactions can be catalyzed either by acidic, basic, or supported noble-metal catalyst. The double-bond migration reactions over noble-metal-supported catalysts reported in the literature consider the

isomerization of methyl linoleate, but not of linoleic acid. The reason for this multistep route could be the slower isomerization rate for carboxylic acids (8). These reactions with methyl linoleate were carried out over rhodium and ruthenium supported by activated carbon between 200 and 270°C (9, 10). Bimetallic ruthenium–nickel catalysts supported by γ - Al_2O_3 , $SiO_2Al_2O_3$, C, and MgO have also been tested at 200°C (11).

The use of linoleic acid as raw material is an attractive alternative to methyl linoleate. Reactions with carboxylic acids over heterogeneous catalysts are difficult to perform, so the question remains if it is possible to carry out the double-bond migration reaction using linoleic acid as a raw material instead of methyl linoleate.

2. EXPERIMENTAL

2.1. Catalyst Synthesis and Characterization Methods

Fluka (Switzerland) supplied 5 wt% Ru/C catalyst. Na-MCM-41 mesoporous molecular sieve was synthesized using a method described elsewhere (12) with some modifications. The reagents tetradecyltrimethylammonium

bromide ($(\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)_3\text{Br})$), aluminium isopropoxide ($([(\text{CH}_3)_2\text{CHO}]_3\text{Al})$), and fumed silica (SiO_2) were supplied by Aldrich. Tetramethylammonium silicate (TMSiO_2) and sodium silicate ($\text{Na}_4\text{O}_4\text{Si}$) were supplied by Sachem and Merck, respectively. A gel mixture was prepared and introduced in a 300-ml autoclave (Parr). The synthesis was carried out in an oven at 200°C for 24 h. After completion of the synthesis, the autoclave was quenched and the mesoporous material was filtered and washed with distilled water. The sample was dried at 110°C and calcined at 550°C . The Na-MCM-41 was ion-exchanged with 1-M NH_4Cl solution, washed with distilled water to remove chloride ions, and dried at 100°C . The H-MCM-41 was obtained by calcination of NH_4 -MCM-41 at 550°C . H-MCM-41 was modified with Ni by an incipient wetness impregnation method using an aqueous solution of nickel nitrate. The H-MCM-41 samples with varied Ni loadings were dried at 100°C and calcined at 450°C for 4 h. The catalytic materials were thereafter sieved to the particle size interval 0–180 μm . The particle size distribution of Ni/H-MCM-41 was measured with sieves.

The calcined Ni/H-MCM-41 catalyst samples were reduced *ex situ* by heating from room temperature to 450°C in flowing hydrogen (100 ml/min) with a heating rate of $10^\circ\text{C}/\text{min}$, and keeping the catalyst at 450°C for 4 h. Thereafter the catalysts were slowly cooled to room temperature before directly admitting exposure to pure air.

X-ray diffraction (XRD) measurements on Ru/C and Ni/H-MCM-41 were performed using a diffractometer (Philips PW 1800) to determine structure, phase purity, and 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° , and counting time 5.0 s per step. The effective crystallite size was measured using the single-line and the approximate methods.

X-ray photoelectron spectroscopy (XPS) measurements on Ni/H-MCM-41 were utilized to analyze the chemical composition of the catalyst surface. Before performing XPS, a calcined catalyst sample and a reduced catalyst sample were preactivated *ex situ* at 180°C under hydrogen in the test reactor to get the same state of reduction as in the catalytic experiments. Thereafter, *n*-decane was fed into the reactor under stirring. The samples were filtered and stored in a special sample holder to avoid exposure to air. The experiments were carried out with a Perkin Elmer PHI 5400 ESCA system. The spectra were excited by the 1253.6-eV unmonochromatized $\text{MgK}\alpha$ X rays with a total instrumental resolution of about 1 eV at the analyzer pass energy of 35.75 eV. The photoelectron emission angle was 30° relative to the sample surface normal. Chamber pressure was below 2×10^{-8} torr during the measurements. The sample charging during the measurements caused a constant en-

ergy shift for all spectral lines, and the binding energy scale was calibrated using the 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.

The Si/Al ratio of MCM was investigated by an X-ray fluorescence spectrometer (Siemens SRS 303) and the BET specific surface areas were measured with an automatic physisorption–chemisorption apparatus (Sorptometer 1900, Carlo Erba Instruments).

Hydrogen storage capacities of the catalysts were investigated by performing hydrogen temperature-programmed desorption (H_2 -TPD) measurements using a volumetric flow apparatus (Autochem 2910, Micrometrics) with nitrogen–argon (N_2 99.5%, Ar 0.5%, AGA) as a carrier gas. In the H_2 -TPD measurements, the Ni was reduced *in situ* by heating from room temperature to 450°C with a heating rate of $10^\circ\text{C}/\text{min}$ in a 50 ml/min 100% hydrogen flow (AGA). The catalyst samples were kept at the reduction temperature in flowing hydrogen for 4 h, cooled to the hydrogen adsorption temperature at a rate of $10^\circ\text{C}/\text{min}$, kept at the adsorption temperature for 1 h, and cooled to 40°C at a rate of $3^\circ\text{C}/\text{min}$ under flowing hydrogen. The hydrogen adsorption temperatures were 100 and 180°C for Ru and Ni, respectively. Thereafter the catalyst was flushed with 50 ml/min N_2/Ar for 45 min. The desorption heating rate was $10^\circ\text{C}/\text{min}$ from 40 to 650°C and the catalyst was kept at 650°C for 30 min. The analyses of the desorbed gases were carried out continuously with a quadrupole mass spectrometer (QTMD, Carlo Erba Instruments). For quantitative measurements, the mass spectrometer was calibrated for the hydrogen signal.

2.2. Isomerization Experiment

Linoleic acid ($\text{C}_{18}\text{H}_{32}\text{O}_2$) of 99% purity was supplied by Fluka (Switzerland). The solvents 1-octanol ($\text{C}_8\text{H}_{18}\text{O}$) of 99.5% purity and *n*-decane ($\text{C}_{10}\text{H}_{22}$) of 95% purity were supplied by Sigma-Aldrich (Germany) and Merck (Germany), respectively. The *trans*-10, *cis*-12, *cis*-9, *trans*-11, *cis*-11, *trans*-13, *cis*-9, *cis*-11, and *trans*-9, *trans*-11 isomers of CLA ($\text{C}_{18}\text{H}_{32}\text{O}_2$) were supplied by Matreya, Inc. (USA). In a typical experiment, the catalyst was charged into a 200-ml stirred batch reactor, which was provided with a reflux condenser and a heating jacket. The catalyst amount was typically 200 mg, but the isomerization reaction was also performed with other catalyst quantities. Silicone oil served as a heat transfer fluid and the reactor was operated at atmospheric pressure. Catalyst preactivation by heating the reactor to the activation temperature in a hydrogen atmosphere started as soon as the catalyst entered the reactor. Isomerization reactions over a catalyst preheated in a nitrogen atmosphere were also performed. The preactivation was carried out *in situ* for 1 h (including heating time) at a hydrogen or nitrogen flow of approximately 100 ml/min.

Ru and Ni catalysts were preactivated at 100 and 180°C, respectively. Linoleic acid (200 mg) was mixed with 70 ml of solvent in a glass tube. The initial concentration of linoleic acid was 0.010 mol/dm³. Air above the reaction mixture and oxygen dissolved in the liquid phase were purged out by a nitrogen flow of 100 ml/min through the reactant solution. A nitrogen flow at the same rate was also fed through the reactor to produce an inert atmosphere while cooling the reactor to the reaction temperature of 80, 100, or 120°C. The liquid phase containing linoleic acid and the solvent was fed into the reactor after a purging time of 20 min and the reaction time was initialized to zero. The temperature of the reflux condensers cooling medium was set to -20°C. Stirring baffles were used inside the reactor. The typical stirring rate was 800 rpm but the isomerization reaction was also conducted at other stirring rates. For calculation of the concentration versus time dependence, samples were withdrawn from the reactor at certain intervals through a sampling valve.

2.3. Analytical Procedure

The samples were silylated and analyzed by a temperature-programmed gas chromatograph (GC) using a 25-m HP-5 column (0.20-mm inner diameter, 0.11- μ m film layer) and a flame ionization detector (FID) operating at 290°C. In the silylation procedure, 10 μ l of samples from the reactor were added into glass tubes that had been washed with methyl *tert*-butyl ether (MTBE, C₅H₁₂O). 50 μ l of 0.5-mg/ml C_{17:0} fatty acid solution was added to each sample to serve as an internal standard for the GC. MTBE and solvent were evaporated in a stream of nitrogen with water as heating medium and the samples were further dried in a vacuum desiccator at 40°C for 20 min. The samples were dissolved in 20 μ l pyridine. Acros Organics supplied 80 μ l N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) of 98% purity and 40 μ l trimethylchlorosilane (TMCS) of 98% purity, which were added to the residue. The solutions were kept in an oven at 70°C for 45 min and were thereafter ready for analysis by GC. The evaporation and silylation operations were conveniently performed with the entire series of samples from one isomerization reaction in parallel to eliminate effects of decomposition. 1- μ l samples were injected into the GC with an autosampler unit using the injector temperature 260°C. Helium served as a carrier gas with a flowrate of 0.9 ml/min and a split ratio of 1 : 20. The column temperature was initially 150°C. The temperature was increased from 150 to 230°C (0.5 min after the injection) with a rate of 7°C/min, and thereafter from 230 to 290°C with a rate of 10°C/min. Thereafter the column was purged at 290°C for 10 min. Peaks corresponding to conjugated dienoic isomers of linoleic acid were identified by injecting the authentic samples. Peak identities were verified by analysis with a gas chromatograph-mass spectrometer (GC/MS) applying the same GC conditions.

3. RESULTS

3.1. Catalyst Characterization

XRD measurements on Na-MCM-41 confirmed that the synthesized mesoporous material had MCM-41 structure. The XRD pattern demonstrated in Fig. 2 exhibits the presence of four peaks, indicating the presence of a hexagonal MCM-41 phase (13). XRD measurements on 5 wt% Ni/H-MCM-41 indicated a reduction of NiO. The crystallite size of the Ni oxide was determined to be 9.89 nm by the approximate method and 9.47 nm by the single-line method. The crystallite size of the metallic Ni was determined to be 5.77 nm by the approximate method and 6.95 nm by the single-line method. The metal particle size of the 5 wt% Ru/C catalyst was higher. According to the approximate method, the Ru crystallite size was determined to be 50.2 nm.

Ni 2p photoelectron spectra of H-MCM-41-supported Ni catalysts from both reduced and calcined states are shown in Fig. 3. The satellite structure in both spectra at the binding energy 861–862 eV is clear evidence that Ni oxides are present. The Ni 2p spectrum of the calcined catalyst is characteristic of the oxides because no spectral structures are present below 855 eV (14). The satellite line positions are about 6 eV to higher binding energies from the main lines, and they can be used as references in the interpretation of the main lines originating from different Ni oxide states, and to estimate the presence of metallic Ni in the catalyst.

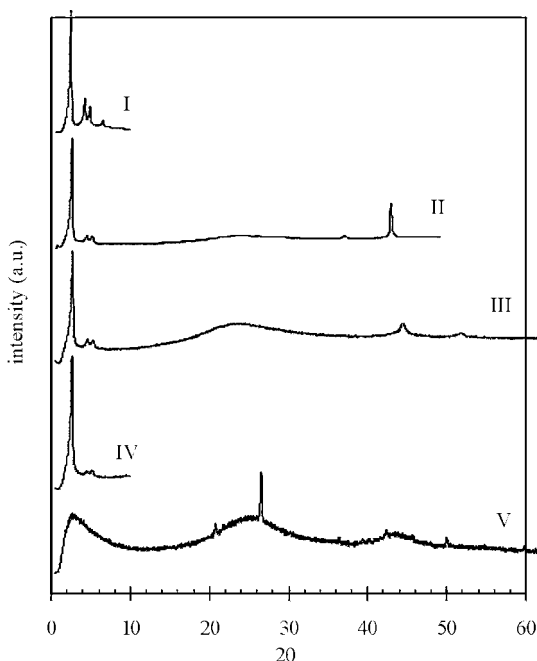


FIG. 2. XRD pattern of (I) Na-MCM-41, (II) calcined 5 wt% Ni/H-MCM-41, (III) calcined and reduced 5 wt% Ni/H-MCM-41, (IV) used 5 wt% Ni/H-MCM-41, and (V) 5 wt% Ru/C.

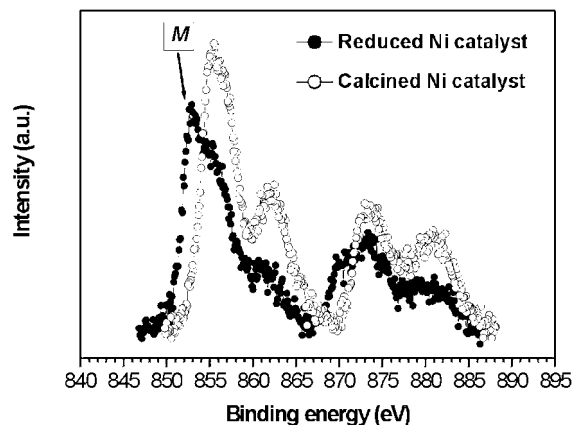


FIG. 3. Ni 2p photoelectron spectra of calcined and reduced 5 wt% Ni/H-MCM-41 samples after background subtracting by Shirley algorithm. The peak originating from metallic nickel is marked by *M*.

The 2p main line of metallic nickel (marked by *M* in Fig. 3) has a binding energy which is more than 2 eV lower than that of the oxides. The satellite structure associated with the metallic nickel spectrum is quite broad and is located in the region between the main and satellite lines of the oxides. In the analysis of the spectra the curve-fitting procedure with the appropriate line shapes was used. The amount of metallic Ni in the reduced catalyst was estimated to be about 30%.

The Si/Al ratio of Na-MCM-41 was determined to be 20 as measured by X-ray fluorescence. BET specific surface area measurements, the pore size distribution, and particle size distribution of the catalytic materials are presented in Tables 1–3. Ni/H-MCM-41 has slightly larger BET area than Ru/C. Ni/H-MCM-41 has a major fraction of pores in the range of 1.0–1.5 nm while Ru/C has larger pores and a fraction of the same magnitude between 10 and 100 nm. It should be noted that approximately only 30% of the MCM-41 pores are larger than 10 nm, which is close to the crystallite sizes of metallic Ni and NiO, as measured by XRD. Hence most of the nickel particles are located on the outer surface of the MCM pores. Table 3 indicates that the particle sizes of 5 wt% Ni/H-MCM-41 are distributed around 71–90 μm but that a large fraction is also present in the interval 0–45 μm . Ru/C has a large fraction of particles in the size intervals 45–63 and 71–90 μm .

TABLE 1

BET Specific Surface Area Measurements

| Catalyst | BET (m^2/g) |
|----------------------------------|-------------------------------|
| 5 wt% Ru/C | 841 |
| 5 wt% Ru/C, used catalyst | 831 |
| Na-MCM-41 | 1214 |
| 5 wt% Ni/H-MCM-41, not reduced | 913 |
| 5 wt% Ni/H-MCM-41, reduced | 1051 |
| 15 wt% Ni/H-MCM-41, reduced | 1021 |
| 5 wt% Ni/H-MCM-41, used catalyst | 77 |

TABLE 2

Pore Size Distributions of Ru/C and Ni/H-MCM-41

| Pore ranges (nm) | Relative volume (%) | |
|------------------|---------------------|-------------------|
| | 5 wt% Ru/C | 5 wt% Ni/H-MCM-41 |
| 0–0.9 | 0 | 0 |
| 0.9–1.0 | 2.6 | 5.2 |
| 1.0–1.5 | 5.9 | 57.2 |
| 1.5–2.0 | 4.2 | 1.5 |
| 2.0–5.0 | 20.8 | 5.3 |
| 5.0–10.0 | 18.1 | 1.3 |
| 10.0–100.0 | 48.4 | 29.6 |

TPD measurements on reduced 5 wt% Ni/H-MCM-41 indicated that as much as 74% of the total amount of adsorbed hydrogen remained on the catalyst surface after a temperature increase to 180°C, which was used as catalyst preactivation temperature for the Ni catalysts. For 5 wt% Ru/C a fraction of 90% of the total hydrogen amount remained on the surface after a temperature increase to 100°C, which was used as preactivation temperature in the catalytic experiments over Ru. The TPD patterns in Fig. 4 indicate spillover hydrogen for both Ru/C and Ni/H-MCM-41. Generally, the amount of spillover hydrogen on the surface of the catalyst support material is proportional to the square root of the catalyst reducing time (15), and its amount increases with reduction temperature.

3.2. Catalytic Activity and Selectivity

The isomerization properties of several supported metal catalysts were investigated. Investigated catalysts were Ru, Ni, Pt, Pd, Rh, Ir, Os, and bimetallic Pt/Rh supported by activated carbon, Al_2O_3 , Al/Si, SiO_2 , MCM-22, H-MCM-41, and zeolites Y and β . After some catalyst screening experiments, it was concluded that Ru, Ni, and Pt have good properties for isomerization of linoleic acid. It became apparent that the activity and the isomerization selectivity were sensitive to the surface structure and hydrogen adsorption capacity of the metal-support combinations. Metals with high hydrogen storage capacity such as Pd showed high

TABLE 3

Particle Size Distributions of Ru/C and Ni/H-MCM-41

| Size ranges (μm) | Mass fraction (%) | |
|-------------------------------|-------------------|-------------------|
| | 5 wt% Ru/C | 5 wt% Ni/H-MCM-41 |
| 0–45 | 6.2 | 22.7 |
| 45–63 | 20.5 | 5.9 |
| 63–71 | 3.3 | 13.7 |
| 71–90 | 31.9 | 23.7 |
| 90–125 | 16.7 | 12.2 |
| 125–150 | 10.6 | 8.7 |
| 150–180 | 10.8 | 13.2 |

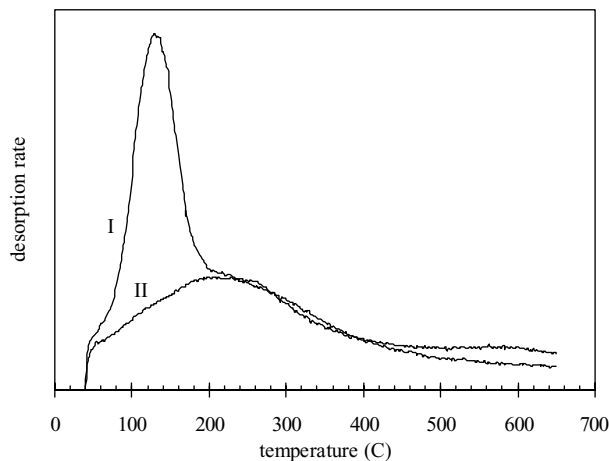


FIG. 4. H₂-TPD profiles: I, 5 wt% Ru/C (H₂ adsorption temperature = 100°C); II, reduced 5 wt% Ni/H-MCM-41 (H₂ adsorption temperature = 180°C).

activity and high selectivity for the double-bond hydrogenation reaction, whereas most of the other tested metals, especially Ru, Ni, and Pt, favored double-bond migration. Very few catalysts, including Ru/C and Ni/H-MCM-41, exhibited feasible conversion. For Ni/Al₂O₃ and Ni/SiO₂, which have much wider pores than MCM-41, more of the metal particles are located inside these pores; however, conversion and isomerization selectivity at the applied standard test conditions were only 10 and 25% for Ni/Al₂O₃ and 43 and 37% for Ni/SiO₂, respectively, after 6 h reaction time. Therefore the Ru/C and Ni/H-MCM-41 catalysts were selected for further studies.

Preliminary isomerization experiments at 120°C in a nitrogen atmosphere over 5 wt% Ru/C, preheated for 1 h at 100°C in pure nitrogen, resulted in 89% selectivity for isomerization. The remaining reaction was hydrogenation (including both monounsaturated and stearic acid). However, the total converted amount of linoleic acid after 6 h was only 11%. In general, protic solvents generate more hydrogen chemisorbed sites on the catalyst surface than nonpolar solvents. In these experiments, *n*-decane was used as the solvent to have no hydrogen in the system and the catalyst quantity was 200 mg. Polymerization, cracking, and geometric or skeletal isomerization of fatty acids were not observed at these conditions. No other reactions were detected except for isomerization of linoleic acid to CLAs and hydrogenation of C_{18:2} fatty acids to C_{18:1} and C_{18:0} fatty acids. Hence, in the following discussion, the term isomerization refers to double-bond migration to form a conjugated system and the sum of the isomerization and hydrogenation selectivities is 1.

Experiments at 100°C in a hydrogen atmosphere over the same Ru/C, preactivated in pure hydrogen, resulted in hydrogenated products. In this case 1-octanol was used as solvent and the catalyst quantity was 50 mg. The concentration versus time dependence for this experiment is pre-

sented in Fig. 5. The mole fraction in the figures refers to the concentration of the specific fatty acid compound relative to the total concentration of fatty acids. The concentration of linoleic acid decreased until the raw material was totally converted. The concentrations of one conjugated dienoic isomer of linoleic acid and monounsaturated acids initially increased with time and started to decrease after reaching a maximum value. The concentration of the conjugated isomer started to decrease earlier than the concentrations of the monounsaturated compounds. The concentration of stearic acid increased monotonically but this product started to build up later than the monounsaturated products. Hydrogenation of linoleic acid to monounsaturated acids and isomerization of linoleic acid are two competing reactions. It can also be concluded that hydrogenation of linoleic acid proceeds consecutively via monounsaturated acids to stearic acid. When the reaction was carried out under hydrogen, no other reactions were detected except for isomerization and hydrogenation.

Despite the fact that the presence of hydrogen leads to hydrogenated products, the isomerization reaction in a nitrogen atmosphere was *dramatically enhanced* when the catalyst was preactivated with hydrogen. When the catalyst was preactivated under hydrogen and the reaction was carried out in 1-octanol over 50 mg of 5 wt% Ru/C in an inert atmosphere (e.g., in the absence of hydrogen) with a nitrogen flow through the reactor, otherwise using the same reaction conditions, the main reaction that took place was isomerization. All reactions in a nitrogen atmosphere were carried out for a specific duration of time (6 h). The overall reaction rate was lower than the rate in the previous experiment in a hydrogen atmosphere, but the isomerization selectivity was higher than the hydrogenation selectivity and only a small trace of stearic acid was formed. The total mole fraction of CLA after 6 h was 33%. The reaction temperature affected the total conversion and the catalyst

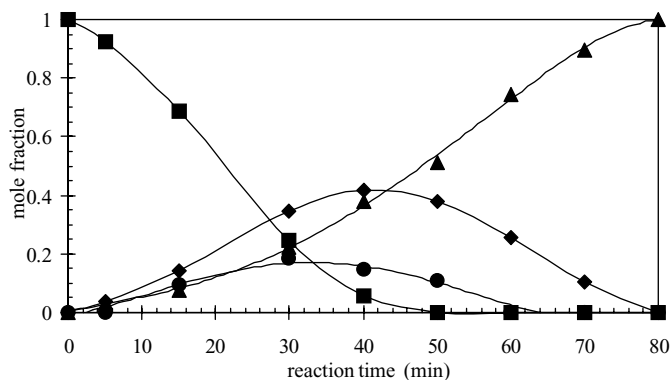


FIG. 5. Kinetic experiment in a hydrogen atmosphere: ■, linoleic acid; ◆, monounsaturated acids; ▲, stearic acid; ●, conjugated dienoic isomer of linoleic acid. Conditions: reaction temperature, 100°C; stirring rate, 800 rpm; solvent, 70 ml 1-octanol; raw material, 200 mg linoleic acid; catalyst, 50 mg 5 wt% Ru/C (preactivated at 100°C for 1 h under hydrogen).

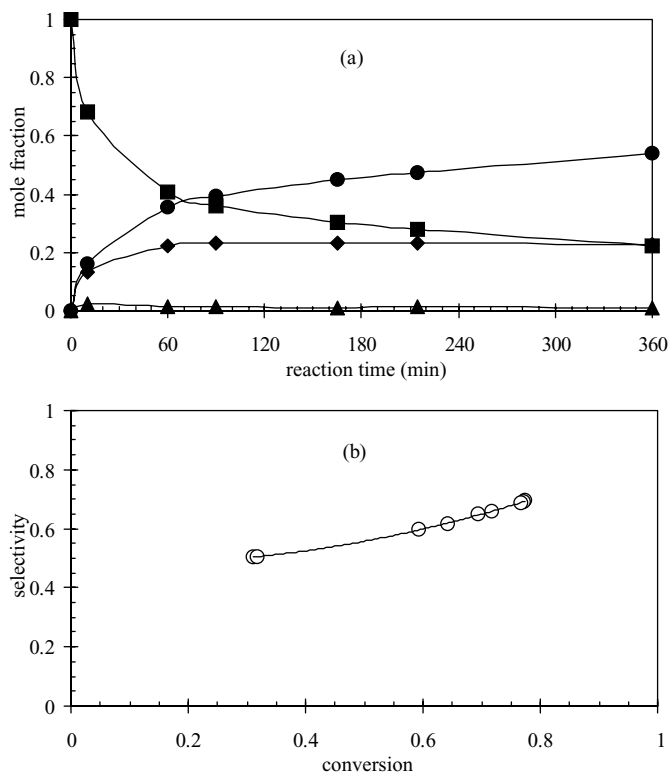


FIG. 6. Kinetic experiment in a nitrogen atmosphere: (a) concentration versus time dependence and (b) selectivity versus conversion dependence. ■, linoleic acid; ◆, monounsaturated acids; ▲, stearic acid; ●, conjugated linoleic acids; ○, selectivity for isomerization. Conditions: reaction temperature, 120°C; stirring rate, 800 rpm; solvent, 70 ml *n*-decane; raw material, 200 mg linoleic acid; catalyst, 200 mg 5 wt% Ru/C (preactivated at 100°C for 1 h under hydrogen).

quantity affected both total conversion and selectivity. The conversion increased from 46 to 53% when the reaction temperature was increased from 100 to 120°C, but the isomerization selectivity was still 74%, resulting in 39 mol% CLA. The isomerization selectivity decreased from 74 to 42% when 200-mg catalyst was used instead of 50 mg, due to the higher hydrogen content of the catalyst. With this larger catalyst quantity the conversion and mole fraction CLA were 78 and 33% respectively. Using *n*-decane instead of 1-octanol, the conversion stayed at 77%, but the isomerization selectivity increased from 42 to 69%, resulting in a yield of 53% conjugation and 24% hydrogenation. The concentration versus reaction time and selectivity versus conversion dependence for this experiment are demonstrated in Fig. 6. The hydrogenation selectivity increases with conversion since the chemisorbed hydrogen generated in the preactivation step is being consumed. In this experiment, the yields of monounsaturated and stearic acids were 23 and 1%, respectively. The H₂ required for the observed hydrogenation is 17.8 mmol/g_{Ru}. The H₂ quantity chemisorbed on the Ru surface according to monolayer adsorption is 9.89 mmol/g_{Ru}, indicating that the spillover hydrogen (Fig. 4) is involved.

The competing isomerization and hydrogenation reactions are influenced by the concentration of chemisorbed hydrogen. If the hydrogen concentration in the solvent is high (as when the reaction is carried out in a hydrogen atmosphere over a catalyst preactivated under hydrogen), the concentration of hydrogen-chemisorbed sites on the catalyst surface will also be high. This increases the rate for the hydrogenation of linoleic acid, consecutively proceeding via monounsaturated acids to stearic acid. If, on the other hand, the concentration of chemisorbed hydrogen is low (as when hydrogen is chemisorbed during the preactivation and consumed during the reaction under a nitrogen pressure), isomerization is preferred over hydrogenation. The fact that isomerization can occur in absence of hydrogen preadsorption is also an important observation.

For comparison, 5 wt% Ni/H-MCM-41 reduced at 450°C in hydrogen for 4 h and preactivated in hydrogen at 180°C for 1 h was tested. Also in this case the reaction was carried out at 120°C in both 1-octanol and *n*-decane to evaluate the effects of a slightly protic and a nonpolar solvent. Figure 7 demonstrates the general trend of results obtained

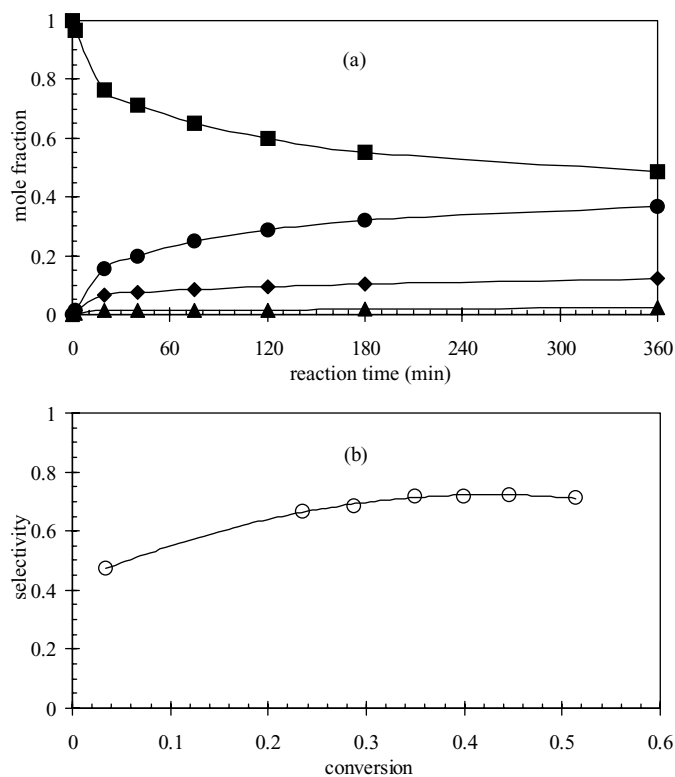


FIG. 7. (a) Concentration versus time dependence and (b) selectivity versus conversion dependence for isomerization of linoleic acid over 5 wt% Ni/H-MCM-41 in *n*-decane. ■, linoleic acid; ◆, monounsaturated acids; ▲, stearic acid; ●, conjugated linoleic acids; ○, selectivity for isomerization. Conditions: reaction temperature, 120°C; stirring rate, 800 rpm; solvent, 70 ml; raw material, 200 mg linoleic acid; catalyst quantity, 200 mg; catalyst particle size interval, 0–180 μm (catalyst reduced and preactivated at 180°C for 1 h under hydrogen).

for 5 wt% Ni/H-MCM-41. The overall reaction rate was high in the beginning of the reaction but decreased with the conversion. After 2 h the concentrations of the fatty acids reached approximately constant values and the consumption rate of linoleic acid was almost zero after a certain period of time. Conversion and selectivities at this point are influenced through a complex connection by (a) the total amount of chemisorbed hydrogen generated in the catalyst preactivation; (b) reaction conditions; (c) deactivation of the catalyst; (d) availability of active vacant sites on the catalyst surface; and (e) competitive adsorption between linoleic acid, solvent, and reaction products. When all hydrogen preadsorbed on the catalyst surface is consumed, the consumption rate of linoleic acid is limited to hydrogen derived from the solvent. In essence, the ease of availability of hydrogen at the catalyst preactivation influences the hydrogen coverage on the catalyst surface. This in turn affects the activity and selectivity pattern observed.

No significant leaching of the impregnated Ni salt by the fatty acids or by the solvent was detected, which indicates that the isomerization and hydrogenation reactions do not occur in the homogeneous phase. The Ni content of the fatty acid solution after a reaction time of 6 h was 10.6 $\mu\text{g/l}$ as determined by direct current plasma atomic emission spectrometry (DCP-AES) (16).

In a catalyst regeneration study, both Ru and Ni catalysts were separated from the fatty acid solution by filtration, washed with acetone in a stirred tank, dried overnight at 100°C, and re-reduced in flowing hydrogen using 400 and 450°C as reduction temperatures for Ru/C and Ni/H-MCM-41, respectively. In the isomerization experiment demonstrated in Fig. 7, the BET area of the Ni/H-MCM-41 catalyst decreased from 1051 to 77 m^2/g and the catalyst was no longer active in a second consecutive experiment. XRD measurements on used Ni/H-MCM-41 (Fig. 2) did not indicate any changes in the MCM structure. It can thus be concluded that a collapse of the structure is not responsible for the deactivation, but blocking of pores and coke formation. The chemical nature of the residue requires a separate study, which is currently being performed. In contrast to Ni/H-MCM-41, Ru/C did not deactivate. When the experiment was carried out over Ru/C, the surface area decreased slightly from 841 to 831 m^2/g , but the catalytic performance did not indicate any deactivation.

When 1-octanol was used as a solvent, the total converted amount of linoleic acid was only 17%, and the isomerization selectivity was only 13%, resulting in 2% conjugation. Although the concentration decrease of linoleic acid was very low, as much as 120 mg of a branched $\text{C}_{20:0}$ compound was formed as a by-product, indicating that 1-octanol is very reactive and not suitable as a solvent in the isomerization reaction of linoleic acid over this particular catalyst. Traces of 3,6-dimethyl octane were also found in the 6-h sample.

When *n*-decane was used as a solvent, the total converted amount of linoleic acid was 51%. The isomerization selec-

tivity was 71 and 29% respectively, resulting in 37% conjugation. The yields of monounsaturated and stearic acids were 12 and 3%, respectively, indicating that the required amount of molecular H_2 for the observed double-bond hydrogenation is 12.8 $\text{mmol/g}_{\text{Ni}}$. The H_2 quantity chemisorbed on the Ni metal surface according to the monolayer adsorption theory is 17.0 $\text{mmol/g}_{\text{Ni}}$, but TPD measurements showed that 70% of the total amount of chemisorbed hydrogen remained on the surface after temperature increase to 180°C, which was used as preactivation temperature, resulting in 11.9 $\text{mmol/g}_{\text{Ni}}$ for monolayer adsorption. It is clear that the hydrogenation is limited to the amount of hydrogen that is chemisorbed in the hydrogen preactivation step. For this particular catalyst, *n*-decane gave higher conversion and higher isomerization selectivity than 1-octanol. This may not be a general rule for other catalysts since experiments over bimetallic platinum-rhodium on carbon in 1-octanol and *n*-decane resulted in higher conversion for 1-octanol. When the reaction was carried out in a nitrogen atmosphere over a hydrogen preactivated catalyst, no other reactions were detected except for isomerization and hydrogenation of linoleic acid.

n-decane was chosen as a solvent for further investigations. For *n*-decane, the overall isomerization rate was higher than the overall hydrogenation rate. A typical pattern for these isomerization reactions in an inert atmosphere over a catalyst preactivated under a pressure of hydrogen is that the yields of monounsaturated acids and stearic acid increase at the beginning of the reaction, and thereafter reach a stable value. The yield of CLA, in turn, typically increases slightly and continuously with the reaction time (as shown in Figs. 6 and 7). The isomerization selectivity, in other words, increases with the conversion and the hydrogenation selectivity decreases with the conversion, once again indicating that the coverage of chemisorbed hydrogen on the catalyst surface affects the isomerization and hydrogenation rates.

3.3. Isomer Distribution

It is clear that the nature of the used solvent affects the isomer distribution. When the isomerization reaction over 5 wt% Ni/H-MCM-41 was performed in *n*-decane as demonstrated in Fig. 7, the 6-h sample included linoleic acid, monounsaturated acids, stearic acid, *trans*-9,*trans*-11, *cis*-9,*trans*-11, *trans*-10,*cis*-12, *cis*-9,*cis*-11 CLA isomers, and six unknown CLA isomers. The composition of fatty acids comprised 49 mol% linoleic acid, 12% monounsaturated acids, 3% stearic acid, and 37% conjugated dienoic isomers of linoleic acid. The distribution of conjugated dienoic isomers was 38% *trans*-9,*trans*-11-CLA, 10% *cis*-9,*trans*-11-CLA, 4% *trans*-10,*cis*-12-CLA, 2% *cis*-9,*cis*-11-CLA, and the remaining 45% unknown conjugated dienoic isomers. Of the CLA obtained, 39% consisted of one single unknown isomer.

When, on the other hand, the isomerization reaction over 5 wt% Ni/H-MCM-41 was performed in 1-octanol, the 6-h sample included linoleic acid, monounsaturated acids, stearic acid, and *cis-9,trans-11*, *trans-9,trans-11*, *trans-10*, *cis-12* CLA isomers. The composition of fatty acids consisted of 83 mol% linoleic acid, 13% monounsaturated acids, 2% stearic acid, and 2% conjugated isomers of linoleic acid. The distribution of conjugated dienoic isomers was 45% *cis-9,trans-11*-CLA, 40% *trans-9,trans-11*-CLA, and 15% *cis-10,cis-12*-CLA.

Ru/C showed higher selectivity toward the *cis-9,trans-11* and *trans-10,cis-12* isomers of CLA (desired products) than Ni/H-MCM-41. When the experiment was conducted over 5 wt% Ru/C in *n*-decane as shown in Fig. 6, the 6-h sample included linoleic acid, monounsaturated acids, stearic acid, *cis-9,trans-11*, *trans-10,cis-12*, *cis-9,cis-11*, *trans-9,trans-11* CLA isomers, and two unknown CLA isomers. The fatty acid composition comprised 23 mol% linoleic acid, 23% monounsaturated acids, 1% stearic acid, and 53% CLA isomers. The CLA isomer distribution was 29% *trans-9,trans-11*-CLA, 24% *cis-9,trans-11*-CLA, 16% *trans-10,cis-12*-CLA, 4% *cis-9,cis-11*-CLA, and the remaining 27% unknown CLA isomers. Of the obtained CLA 26% consisted of a single unknown isomer. The selectivities toward specific isomers of CLA did not depend on the reaction time or the conversion.

3.4. Effect of Reaction Temperature

Activity and selectivity data on Ni/H-MCM-41 catalyst are reported in Table 4. The total converted amount of

linoleic acid increased with temperature, but the selectivities for isomerization and hydrogenation were not strongly affected by the temperature. The selectivities alternated around 70% for isomerization and 30% for hydrogenation at varied reaction temperature. The total conversion and conjugation increased from 11 and 7% to 51 and 37%, respectively, when the temperature was increased from 80 to 120°C. The reaction temperature did not affect the selectivities for specific isomers of CLA.

3.5. Effect of Catalyst Reduction

The surface area of calcined 5 wt% Ni/H-MCM-41 increased from 913 to 1051 m²/g when the catalyst was reduced in a hydrogen flow at 450°C for 4 h. Conversion and selectivities were not strongly affected by the Ni reduction. TPR studies on Ni/Al₂O₃, Ru/Al₂O₃, Ru/SiO₂, and Ru/Na-Y (17, 18) have shown that after oxygen treatment, Ru/Na-Y already started to consume H₂ at 100°C, whereas the hydrogen uptake started at 180 to 200°C for Ru/Al₂O₃ and Ru/SiO₂, and the catalysts were easily fully reduced. Oxidic Ni catalysts with varied Ni loading showed a broad H₂ consumption range of 230 to 580°C with a maximum at 380°C, but TPR profiles on Ni catalysts pretreated with high-temperature reduction and passivation in nitrogen-diluted oxygen showed a maximum H₂ consumption at 270°C. The integrated hydrogen consumption was quantified and normalized to the Ni content. Assuming that the stoichiometry of nickel oxide is NiO, the reduction degree of the reduced and passivated Ni catalysts was in the range of 28–40%.

TABLE 4
Activity and Selectivity Data on Ni/H-MCM-41 for Isomerization of Linoleic Acid

| Solvent | Reaction temp. (°C) | Metal loading (wt%) | Cat. mass (mg) | Particle size (μm) | Catalyst reduction | Initial conc. (mol dm ⁻³) | Conv. ^a (%) | Conj. ^b (%) | Hydr. ^c (%) | S _I ^d | S _H ^e | Initial rate ^f (×10 ⁻⁷ mol s ⁻¹ g ⁻¹) |
|------------------|---------------------|---------------------|----------------|--------------------|--------------------|---------------------------------------|------------------------|------------------------|------------------------|-----------------------------|-----------------------------|--|
| <i>n</i> -decane | 120 | 5 | 200 | 0–180 | No | 0.01 | 56 | 40 | 16 | 0.71 | 0.29 | 3.8 |
| <i>n</i> -decane | 120 | 5 | 200 | 0–180 | Yes | 0.01 | 51 | 37 | 15 | 0.71 | 0.29 | 3.2 |
| <i>n</i> -decane | 120 | 5 | 200 | 45–63 | Yes | 0.01 | 34 | 25 | 9 | 0.73 | 0.27 | 1.4 |
| <i>n</i> -decane | 120 | 0 | 200 | 45–63 | Yes | 0.01 | 22 | 16 | 6 | 0.71 | 0.29 | 0.9 |
| <i>n</i> -decane | 120 | 15 | 200 | 45–63 | Yes | 0.01 | 64 | 45 | 19 | 0.70 | 0.30 | 3.9 |
| <i>n</i> -decane | 120 | 5 | 400 | 0–180 | Yes | 0.01 | 72 | 41 | 25 | 0.57 | 0.43 | 2.6 |
| <i>n</i> -decane | 100 | 5 | 200 | 0–180 | Yes | 0.01 | 22 | 15 | 7 | 0.70 | 0.30 | 1.0 |
| <i>n</i> -decane | 80 | 5 | 200 | 0–180 | Yes | 0.01 | 11 | 7 | 4 | 0.64 | 0.36 | 0.6 |
| <i>n</i> -decane | 120 | 5 | 200 | 0–180 | Yes | 0.005 | 70 | 42 | 28 | 0.60 | 0.40 | 2.6 |
| 1-octanol | 120 | 5 | 200 | 0–180 | Yes | 0.01 | 17 | 2 | 15 | 0.13 | 0.87 | 1.4 |

Note. Conditions: raw material, linoleic acid; solvent quantity, 70 ml; stirring rate, 800 rpm; reaction pressure, 1 atm of nitrogen; hydrogen adsorption time, 1 h; hydrogen adsorption temperature, 180°C; reaction time, 6 h.

^a All percentages refer to mole percentages.

^b Includes all CLA isomers.

^c Includes both monounsaturated acids and stearic acids.

^d Selectivity for isomerization: S_I = conjugation/total conversion.

^e Selectivity for hydrogenation: S_H = hydrogenation/total conversion.

^f Based on total converted amount of linoleic acid after 60 min and catalyst mass.

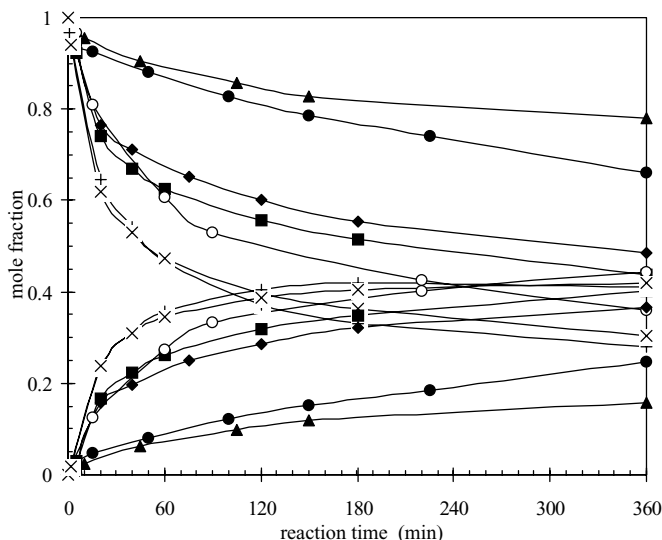


FIG. 8. Influence on concentration decrease of linoleic acid and yield of CLA of varied Ni loading, catalyst particle size, catalyst quantity, initial concentration of linoleic acid, and reduction state of Ni. ■, 5 wt% Ni, 0–180 μm , 200-mg not-reduced catalyst, $c_0 = 0.01 \text{ mol/dm}^3$; ◆, 5 wt% Ni, 0–180 μm , 200-mg reduced catalyst, $c_0 = 0.01 \text{ mol/dm}^3$; ▲, no metal, 45–63 μm , 200-mg reduced catalyst, $c_0 = 0.01 \text{ mol/dm}^3$; ●, 5 wt% Ni, 45–63 μm , 200-mg reduced catalyst, $c_0 = 0.01 \text{ mol/dm}^3$; ○, 15 wt% Ni, 45–63 μm , 200-mg reduced catalyst, $c_0 = 0.01 \text{ mol/dm}^3$; +, 5 wt% Ni, 0–180 μm , 400-mg reduced catalyst, $c_0 = 0.01 \text{ mol/dm}^3$; ×, 5 wt% Ni, 0–180 μm , 200-mg reduced catalyst, $c_0 = 0.005 \text{ mol/dm}^3$. Conditions: reaction temperature, 120°C; stirring rate, 800 rpm; solvent, 70 ml *n*-decane (catalyst preactivated at 180°C for 1 h under hydrogen).

3.6. Effect of Catalyst Particle Size

The selectivities for isomerization and hydrogenation were also not strongly affected by the catalyst particle size but the total conversion decreased from 51 to 34% when the particle size interval of the 5 wt% Ni/H-MCM-41 was narrowed from 0–180 μm to 45–63 μm as demonstrated in Fig. 8. The initial overall reaction rate based on conversion at 60 min and catalyst mass decreases dramatically from 3.2×10^{-7} to $1.4 \times 10^{-7} \text{ mol s}^{-1} \text{ g}^{-1}$. The reason for this decrease in conversion and initial rate might be that the fraction with particle sizes less than 45 μm (as much as 23 mass%, as reported in Table 3) was removed, indicating that internal diffusional limitations exist. The particle size does not affect selectivities for specific CLA isomers.

3.7. Effect of Catalyst Metal Loading

The BET area decreased as the metal loading was increased. Considering 0, 5, and 15 wt% Ni, the initial overall reaction rate was proportional to the catalyst metal loading. The effect of loading of Ni on the support material was studied by using a very narrow catalyst particle size interval (45–63 μm). A special experiment was carried out with the proton form, H-MCM-41, to investigate the catalytic properties of the support material. Figure 8 also demonstrates

how conversion and yield of CLA increased when the catalyst metal loading was increased. Selectivities for isomerization and hydrogenation were not strongly affected by the loading, but the linoleic acid converted after 6 h is a linear function of the Ni loading with an R-squared value of 0.99. No changes in selectivities for specific isomers of CLA were detected as the metal loading was varied.

3.8. Effects of Catalyst Quantity

The total converted amount of linoleic acid over reduced 5 wt% Ni/H-MCM-41 at 6 h increased from 51 to 72% when 400-mg catalyst was used instead of 200 mg at the same reaction conditions, but the isomerization selectivity decreased from 71 to 57% because there was more adsorbed hydrogen available for the competing hydrogenation reaction, resulting in an increase of the yield of conjugated linoleic acids from 37 to 41% as demonstrated in Fig. 8. The initial overall reaction rate was practically the same ($3.2 \times 10^{-7} \text{ mol s}^{-1} \text{ g}^{-1}$ and $2.7 \times 10^{-7} \text{ mol s}^{-1} \text{ g}^{-1}$) as 200 mg reduced 5 wt% Ni/H-MCM-41 was changed to 400 mg, but the concentration of linoleic acid as a function of the reaction time decreased more rapidly for the higher catalyst quantity. The catalyst mass did not affect the selectivities for specific isomers of CLA. The dissolubility of Ni in the fatty acid solution after the 6-h reaction time was still low at the 400-mg catalyst mass level. The concentration of Ni in the liquid phase was only 8.7 $\mu\text{g/l}$ as indicated by DCP-AES measurements.

3.9. Effect of Initial Linoleic Acid Concentration

The reactant mass to catalyst mass ratio was decreased by 50% because 400-mg catalyst was used instead of 200 mg. This ratio was also decreased by 50% because the initial linoleic acid concentration was decreased from 0.010 to 0.005 mol/dm^3 . The converted linoleic acid over reduced 5 wt% Ni/H-MCM-41 at 6 h increased from 51 to 70% when 100 mg of linoleic acid was used instead of 200 mg at the same reaction conditions, but the isomerization selectivity decreased from 71 to 60% due to the higher amount of hydrogen in the system relative to the amount of the reactant, resulting in an increase of the yield of conjugated linoleic acids from 37 to 42%. It should be noted that the same conversion and selectivities could be obtained by either increasing the catalyst mass or decreasing the reactant mass by a factor of 2, as expected.

3.10. Effects of Agitation

Influence of agitation was experimentally determined by varying the stirring rate. The isomerization reaction was carried out at 400, 600, 800, and 1000 rpm, otherwise using the same reaction conditions. Catalytic activity, selectivities toward isomerization and hydrogenation, and the initial overall reaction rate at these stirring speeds are presented

TABLE 5
Activity and Selectivity Data on Reduced Ni/H-MCM-41
at Varied Stirring Rate

| Stirring rate (rpm) | Conv. (%) | Conj. (%) | Hydr. (%) | S_C | S_H | Initial overall reaction rate ($\times 10^{-7}$ mol s^{-1} g^{-1}) |
|---------------------|-----------|-----------|-----------|-------|-------|--|
| 400 | 45 | 32 | 13 | 0.72 | 0.28 | 3.4 |
| 600 | 54 | 34 | 20 | 0.64 | 0.36 | 4.5 |
| 800 | 45 | 32 | 12 | 0.72 | 0.28 | 3.1 |
| 1000 | 52 | 34 | 18 | 0.65 | 0.35 | 4.1 |

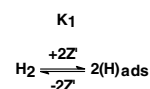
Note. Conditions: raw material, 200 mg linoleic acid; solvent, 70 ml *n*-decane; reaction temperature, 120°C; Ni loading, 5 wt%; catalyst mass, 200 mg; catalyst particle size interval, 0–180 μ m; reaction pressure, 1 atm of nitrogen; hydrogen adsorption time, 1 h; hydrogen adsorption temperature, 180°C; reaction time, 3 h.

in Table 5. It is clear from these results that the diluted system is well mixed and it is obvious that all isomerization experiments were performed on the plateau of the initial rate against the stirring rate.

4. DISCUSSION

The double-bond migration reaction over a hydrogen preactivated catalyst is thought to occur via the Horiuti-Polanyi mechanism (19) describing hydrogenation and isomerization of olefins. A schematic representation of a possible reaction network for a catalyst preactivated under hydrogen is demonstrated in Fig. 9. H_2 , Z , Z' , $Z'H$, C_2 , C_{2i} , C_1 , C_0 , C_2H , and C_1H denote hydrogen, active vacant surface site for chemisorption of organic molecule, active vacant surface site for chemisorption of hydrogen, hydrogen chemisorbed site, linoleic acid, conjugated linoleic acids, monounsaturated acids, stearic acid, half-hydrogenated intermediate species derived from diunsaturated acids, and half-hydrogenated intermediate species

chemisorption of hydrogen



conversion of linoleic acid

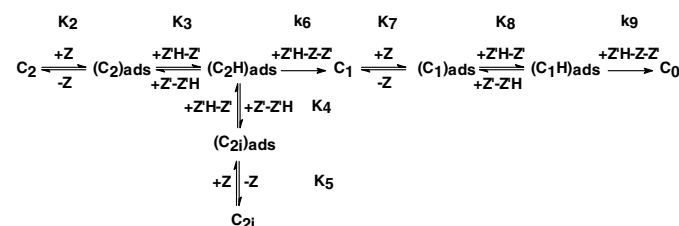


FIG. 9. Schematic representation of a possible reaction network for a catalyst preactivated under hydrogen.

derived from monounsaturated acids, respectively. $(C_i)_{ads}$ denotes chemisorbed organic molecule i , etc. After preactivation under hydrogen (step 1) initially the compound containing one or two double bonds is chemisorbed on the surface of the metal or on the surface of the support material for the case with no metal loading (step 2). Thereafter, a hydrogen atom derived from a hydrogen chemisorbed site is added to the chemisorbed acid to give a chemisorbed half-hydrogenated intermediate (step 3). If the hydrogen coverage on the catalyst surface is low (as at the end of the reaction when conjugation is preferred), hydrogen abstraction by the metal takes place from an adjacent carbon atom (step 4). This could lead to a double-bond migration depending on which carbon atom the hydrogen is abstracted from. Thereafter the chemisorbed product is desorbed from the surface of the catalyst metal or the support material (step 5). On the other hand, if the coverage of hydrogen is high (as in the beginning of the reaction when hydrogenation is preferred over isomerization), a second hydrogen atom is added to the chemisorbed half-hydrogenated intermediate (step 6), leading to a hydrogenated product. In essence the addition of hydrogen to olefins are surface reactions involving the addition of chemisorbed hydrogen to chemisorbed olefins. Steps 3 and 6 correspond to addition of two hydrogen atoms to the same side of the chemisorbed olefin (*cis*-addition). We have chosen to model step 6 as an irreversible reaction since this step is almost irreversible for hydrogenation of olefins at low temperatures.

An explanation of the fact that double-bond migration also occurs in total absence of hydrogen must be given. As much as 89% of the converted linoleic acid contributed to the yield of CLA at a conversion of 11% when the isomerization reaction was carried out in absence of hydrogen. In this case the solvent is assumed to generate hydrogen chemisorbed sites. The reason for the high selectivity toward isomerization in absence of preactivation is the low concentration of chemisorbed hydrogen. For a catalyst preactivated under hydrogen, we can assume that an equilibrium concentration of chemisorbed hydrogen on the catalyst surface is reached during the activation, hence the chemisorbed hydrogen generated during the preactivation is the hydrogen source in the beginning of the reaction. A negligible noncatalytic direct hydrogenation of linoleic acid proceeding consecutively via monounsaturated acids to stearic acids also occurs. The hydrogen source for this direct hydrogenation is the solvent and the rate is influenced by the nature of the solvent.

No changes in the distribution between specific CLA isomers were detected by varying reaction temperature, catalyst reduction, catalyst particle size interval, metal loading, catalyst quantity, initial linoleic acid concentration, or stirring rate. Based on the obtained data, activity and selectivity can be treated separately. The total converted amount of linoleic acid was affected by reaction temperature, catalyst

metal loading, catalyst quantity, initial linoleic acid concentration, catalyst particle size, and nature of the solvent. An increase of reaction temperature, metal loading, and catalyst quantity, and a decrease of initial linoleic acid concentration and particle size resulted in higher total conversion, and *n*-decane showed higher conversion than 1-octanol. The selectivities toward isomerization and hydrogenation on the other hand were affected only by catalyst quantity, initial linoleic acid concentration, and nature of the solvent. An increase of the catalyst mass or a decrease of the initial linoleic acid concentration resulted in a decrease of the isomerization selectivity due to the hydrogen storage capacity of the catalyst, and *n*-decane showed very high isomerization selectivity compared to 1-octanol. Also, selectivities for specific CLA isomers were affected by the solvent.

Considering the second step in Fig. 9, the nature of the solvent might be affecting the adsorption equilibrium and thereby the coverage of linoleic acid and the total amount of adsorbed linoleic acid. A nonpolar solvent might be preferred for having a maximum adsorption of linoleic acid on the catalyst surface due to less strong competitive adsorption between linoleic acid and solvent. Poor adsorption of linoleic acid leads to a lower coverage of chemisorbed half-hydrogenated intermediate species. A lower intermediate coverage in turn favors hydrogenation, since the ratio between intermediates and chemisorbed hydrogen in this case is lower. It is possible that this fact contributed to the changes in the selectivities toward isomerization and hydrogenation when the isomerization reaction was performed in 1-octanol and *n*-decane. A nonpolar solvent might also provide a better solvation of linoleic acid.

Another parameter that has a definite influence on the second step in Fig. 9 is the catalyst metal loading. An increase of the metal loading results in an increase of the total amount of chemisorbed linoleic acid. Even the reaction temperature and the catalyst mass affect the amount of chemisorbed linoleic acid. The total amount of active sites is increased by an increase of the catalyst mass, resulting in an increase of the amount of chemisorbed linoleic acid. The reaction temperature, in turn, affects the adsorption isotherm. However, the fractional surface coverage is not affected by catalyst metal loading or catalyst mass.

Considering the third step in Fig. 9, where a hydrogen atom derived from a hydrogen chemisorbed site is added to the adsorbed organic molecule, the rate is determined by the coverage of hydrogen and the coverage of linoleic acid. The total amount of hydrogen is increased by an increase of metal loading and catalyst mass, but the fractional surface coverage of hydrogen is not affected by these parameters.

The hydrogen addition and hydrogen abstraction in the fourth and the sixth steps in Fig. 9 are affected by the coverage of hydrogen and the coverage of half-hydrogenated intermediate species. Conjugation is favored by high intermediate coverage and low hydrogen coverage.

In fact, the catalyst metal loading affects the initial overall reaction rate but not the selectivities. It is thus understandable that the conversion at a reaction time of 6 h is a linear function of the metal loading, since an increased metal loading increases the total amount of hydrogen generated in the catalyst preactivation and the total amount of chemisorbed half-hydrogenated intermediate species. The reason for the constant selectivities might be that the ratio between coverage of intermediates and coverage of hydrogen is not greatly affected by the metal loading, and that the total amount of chemisorbed hydrogen generated in the preactivation is not dramatically changed. The hydrogen rate increases dramatically compared to the isomerization rate when the catalyst mass is increased. The reason for this might be that the total amount of chemisorbed hydrogen generated in the preactivation increases more when the catalyst mass is increased compared to the case with increased metal loading, since not only the catalyst metal is involved in the hydrogen storage, but also the support material.

The Horiuti–Polanyi mechanism was suggested earlier (9) in the case of isomerization of methyl linoleate over carbon-supported Rh and Ru catalysts and the mechanism is supported by our results. The kinetics of the isomerization of methyl linoleate were studied between 200 and 270°C under nitrogen (9). Reactions taking place were double-bond migration, hydrogenation, and polymerization. It was concluded that the hydrogenation was caused essentially by hydrogen derived from the solvent, and that activity and selectivities were dependent on the solvent used. Highly protic solvents like methanol or isopropyl alcohol exhibited high activity and high hydrogenation selectivity, whereas aprotic solvents like hexane or cyclohexane showed high isomerization selectivity. It was also concluded that low solvent concentration, high catalyst quantity, and high reaction temperature favor polymer formation, that the isomer distribution was affected by both reaction time and reaction temperature, and that activity and selectivities could be manipulated by varying the solvent compositions. But in Deshpande *et al.* (9) and in similar studies of the isomerization reaction of methyl linoleate (10, 11), the hydrogenation reaction of methyl linoleate was believed to be consecutive proceeding via the conjugated isomer. (Conjugation was followed by hydrogenation to monounsaturated species with no parallel hydrogenation of methyl linoleate.)

The isomerization reaction of linoleic acid to conjugated linoleic acids can also take place through several other routes. 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 (20). Acid-catalyzed isomerization may also occur on NiO sites.

5. CONCLUSIONS

A new heterogeneously catalytic pathway was developed for isomerization of linoleic acid to CLAs at mild reaction conditions over Ru/C and Ni/H-MCM-41 catalysts, which is the first report on the isomerization of this acid but not its ester, over heterogeneous catalysts. The major finding is summarized as follows. The isomerization of linoleic acid to CLA and the hydrogenation of linoleic acid and CLA are two competing parallel reactions. Hydrogenation of linoleic acid and CLA proceeds consecutively via monounsaturated octadecenoic acids to stearic acid. Isomerization can occur through a Brønsted acid catalyzed pathway, an allylic dehydrogenation pathway, or through half-hydrogenated intermediates. The concentrations of chemisorbed hydrogen and key intermediates on the catalyst surface have a definite influence on catalytic activity and selectivities toward isomerization and hydrogenation through a complex relation. A low concentration of chemisorbed hydrogen on the catalyst surface favors isomerization while a high concentration favors hydrogenation; however, chemisorbed hydrogen increases the isomerization reaction rate. Therefore the isomerization can be enhanced if the reaction is carried out in a nitrogen atmosphere over a catalyst preactivated under a pressure of hydrogen compared to the case when chemisorbed hydrogen is derived from the solvent. Ru/C exhibits higher selectivity toward *cis*-9,*trans*-11-CLA and *trans*-10,*cis*-12-CLA than Ni/H-MCM-41. When the reaction is carried out in an inert atmosphere over a catalyst preactivated in hydrogen, the total conversion is affected by several parameters such as reaction temperature, catalyst metal loading, catalyst quantity, initial linoleic acid concentration, catalyst particle size, and nature of the solvent, but the selectivities toward isomerization and hydrogenation are affected only by catalyst quantity, initial linoleic acid concentration, and nature of the solvent. Formation of *trans* bonds is preferred over formation of *cis* bonds, but selectivities toward individual CLA isomers can be affected by using different solvents.

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