# Design of Ru–Zeolites for Hydrogen-Free Production of Conjugated Linoleic Acids

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While conjugated vegetable oils are currently used as additives in the drying agents of oils and paints, they are also attractive molecules for making bio-plastics. Moreover, conjugated oils will soon be accepted as nutritional additives for "functional food" products. While current manufacture of conjugated vegetable oils or conjugated linoleic acids (CLAs) uses a homogeneous base as isomerisation catalyst, a heterogeneous alternative is not available today. This contribution presents the direct production of CLAs over Ru supported on different zeolites, varying in topology (ZSM-5, BETA, Y), Si/Al ratio and countercation (H<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup>). Ru/Cs-USY, with a Si/Al ratio of 40, was identified as the most active and selective catalyst for isomeri-

Introduction

The term conjugated linoleic acids (CLAs) encompasses all positional and geometric isomers of conjugated linoleic acid. This acid is a major component in vegetable oils. Soya bean and safflower oil typically contain linoleic acid levels up to 53.7 and 77.7%, respectively.<sup>[1]</sup> Linoleic acid has two double bonds, both in the *cis* configuration, located at positions 9 and 12, whereas CLAs have two conjugated double bonds, with either *cis* or *trans* configurations, located at various positions. Traditionally, adding CLAs to coatings and paints improves the drying properties.<sup>[2]</sup> Because conjugated double bonds are more reactive than unconjugated ones, CLAs are also used as co-monomers in the production of bio-plastics by cationic and free-radical copolymerisation.<sup>[3]</sup> Highly productive and sustainable processes are key challenges for industrial CLA usage.

In recent years, a variety of positive health effects have been attributed to CLAs. They are claimed to be anticarcinogenic, antidiabetic, antioxidative and antiarteriosclerotic. They decrease fat and increase muscle content in the body, reduce inflammation, show a beneficial effect on bone formation, enhance immune functions and reduce asthma.<sup>[4]</sup> However, from the 56 theoretically possible CLA isomers, only specific isomers, namely, cis-9,trans-11-CLA and trans-10,cis-12-CLA show such properties. More recent research indicates that trans-9, trans-11-CLA also exhibits beneficial health effects, superior to the more abundantly present cis-9, trans-11- and trans-10, cis-12-CLA.<sup>[5]</sup> Of all CLA isomers, cis-9,trans-11-CLA is by far the most dominant in food products (up to 90% of the total CLA content), especially in milk and tissue fats of ruminants, where it is synthesised from linoleic acid by rumen bacteria.<sup>[6]</sup> Whereas the daily dietary uptake of CLA is only 0.10-0.43 g,<sup>[7]</sup> the occurrence of sation of methyl linoleate (*cis*-9,*cis*-12 (C18:2)) to CLA at 165 °C. Interestingly, no hydrogen pre-treatment of the catalyst or addition of hydrogen donors is required to achieve industrially relevant isomerisation productivities, namely, 0.7 g of CLA per litre of solvent per minute. Moreover, the biologically most active CLA isomers, namely, *cis*-9,*trans*-11, *trans*-10,*cis*-12 and *trans*-9,*trans*-11, were the main products, especially at low catalyst concentrations. Ex situ physicochemical characterisation with CO chemisorption, extended X-ray absorption fine structure measurements, transmission electron microscopy analysis, and temperature-programmed oxidation reveals the presence of highly dispersed RuO<sub>2</sub> species in Ru/Cs-USY(40).

advantageous effects in humans requires daily uptake levels of about 3 g.<sup>[8]</sup> Therefore, enhanced CLA uptake, leading to beneficial effects on human health, would require the addition of CLA to functional food products.

Today, the industrial production of CLA involves high-temperature catalysed isomerisation of vegetable oils (rich in linoleic acid) or fatty acids, such as linoleic acid, with homogeneous bases, namely, potassium hydroxide or potassium alcoholates, using solvents, namely, ethylene glycol.<sup>[9]</sup> Subsequent neutralisation with an acid, namely, phosphoric acid, is necessary. In this way, almost equal amounts of *cis-9,trans-11-* and *trans-10,cis-12-*CLA isomers are formed with high productivity and selectivity (Table 1, entries 1 and 2). Unfortunately, the present commercial production of CLAs, requiring the use of dissolved alkali, solvents and acid addition, does not show the characteristics of a sustainable process. Moreover, CLA-enriched triacylglycerols or methyl esters cannot be obtained directly with homogeneous bases because they hydrolyse ester

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Entry	Substrate	Catalyst	Solvent	<i>T</i> [°C]	RA	$Y_{CLA}^{[a]}$	$P^{[b]}$	$R^{[c]}$	TOF <sup>[d]</sup>	Ref.
1	methyl linoleate	КОН	ethylene glycol	180	N <sub>2</sub>	97	0.63	-		[30]
2	safflower FAME	KOCH <sub>3</sub>	methanol	111–115	N <sub>2</sub>	70	6.69	-	-	[9a]
3	methyl linoleate	Ru/C	cyclohexane	230	$N_2$	34	0.021	15.0	6.4	[12a]
4	methyl linoleate	Ru/C	hexane	250	$N_2$	31	0.019	13.6	5.3	[12a]
5	linoleic acid	Ru/C	<i>n</i> -decane	120	N <sub>2</sub> <sup>[e]</sup>	53	0.004	1.8	0.9	[12b], [12h]
6	linoleic acid <sup>[f]</sup>	Ru/C	/	165	$N_2$	58	0.90	23	17.2	[31]
7	linoleic acid	Ru/Al <sub>2</sub> O <sub>3</sub>	<i>n</i> -decane	120	N <sub>2</sub> <sup>[e]</sup>	28	0.002	0.9	0.5	[12h]
8	linoleic acid	Ru/H-Y	<i>n</i> -decane	120	N <sub>2</sub> <sup>[e]</sup>	24	0.002	0.8	0.4	[12h]
9	linoleic acid	Ru/H-β	<i>n</i> -decane	120	N <sub>2</sub> <sup>[e]</sup>	36	0.003	1.2	0.6	[12h]
10	linoleic acid	Ag/SiO <sub>2</sub>	<i>n</i> -decane	165	H <sub>2</sub>	67	0.021	1.5	0.7	[12d]
11	linoleic acid	Au/TS-1	<i>n</i> -decane	165	Н,	33	0.002	0.7	1.4	[12f]
12	linoleic acid	Au/C	<i>n</i> -decane	150	H <sub>2</sub>	4	0.0005	0.2	0.1	[12f]
13	methyl linoleate	Ru/Cs-USY	<i>n</i> -decane	165	$N_2$	67	0.698	419	175.5 <sup>[g]</sup>	this work
14	methyl linoleate	Ru/Cs-USY	<i>n</i> -decane	165	N <sub>2</sub>	75	0.391	234	99.8 <sup>[h]</sup>	this work

linkages.<sup>[9a,10]</sup> Homogeneous isomerisation using transitionmetal complexes has also been studied and allows almost quantitative conversion of linoleic acid to CLAs.<sup>[11]</sup> Despite the high CLA selectivity, separation of the catalyst from the substrate remains delicate.

Heterogeneous catalysis constitutes an attractive strategy for sustainable CLA production because the catalyst can be separated and reused easily. Although some heterogeneous processes for isomerisation of linoleic acid or methyl linoleate have already been described in the literature,<sup>[12]</sup> low productivity is the main drawback (Table 1, entries 3–12). Moreover, it was concluded that low amounts of hydrogen, present as chemisorbed hydrogen atoms on the metal surface, were required to perform the isomerisation reaction at an acceptable rate. Too much hydrogen caused the formation of an excess of unwanted hydrogenated products (Scheme 1). To suppress the hydrogenation reaction, a two-step process was used in which the ruthenium catalyst was first covered with hydrogen. In the



Scheme 1. Isomerisation/hydrogenation of linoleic acid with a heterogeneous catalyst.

second step, linoleic acid was isomerised to CLA in a nitrogen atmosphere.<sup>[12b,c]</sup> Although the selectivity for conjugation was higher than for hydrogenation, significant quantities of hydrogenated products, especially oleic acid, were formed. Indeed, with a Ru/C catalyst, pre-activated under hydrogen, 53% conjugation and 24% hydrogenation was achieved after 6 h at 120 °C. When the pre-activation step was omitted, the catalyst activity was reduced significantly. Ru on alumina and zeolite catalysts, prepared by incipient wetness impregnation of ruthenium acetyl acetonate and RuCl<sub>3</sub>, respectively, also show rather low rates of CLA productivity, comparable to that of Ru/C.<sup>[12g,h]</sup> Silver- and gold-based heterogeneous catalysts were also tested in the isomerisation of linoleic acid in presence of hydrogen. Because these metals have low hydrogen-binding energies, low selectivity for hydrogenated products was obtained.<sup>[12d, e]</sup>

In view of this, the design of a heterogeneous catalyst with high activity towards the formation of the physiologically important *cis*-9,*trans*-11-, *trans*-10,*cis*-12- and *trans*-9,*trans*-11-CLA isomers, and with a low activity towards the formation of other CLA isomers and hydrogenated products, remains a challenge. We describe herein a new isomerisation catalyst for the synthesis of CLAs in the absence of hydrogen, using a Ru/USY catalyst with high Ru dispersion. While almost no hydrogenated products are formed, high productivity of and selectivity for beneficial CLAs is achieved.

### **Results and Discussion**

### Support influence

Different zeolite supports were loaded with ruthenium and tested in the isomerisation of methyl linoleate (Table 2). The zeolites tested differ in topology (MFI (ZSM-5), BEA (BETA), FAU (Y)), Si/Al ratio (2.5–180) and countercation (H<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup>). The results of a commercial Ru/C catalyst are incorporated as a reference. During the isomerisation of methyl linoleate, four types of products are formed, namely, conjugated (CLA) and

Table 2. Catalytic properties of supported ruthenium catalysts for the isomerisation of methyl linoleate (ML) <sup>[a]</sup> .												
Entry	Support	Si/Al	$A_i^{[b]} \times 10^{-5}$ [mol min <sup>-1</sup> ]	t [min]	X <sub>ML</sub> <sup>[c]</sup> [%]	Y <sub>CLA</sub> <sup>[d]</sup> [wt %]	S <sub>CLA</sub> <sup>[e]</sup> [%]	S <sub>ct</sub> <sup>[f]</sup> [%]	S <sub>tt</sub> <sup>[g]</sup> [%]	S <sub>HP</sub> <sup>[h]</sup> [%]	S <sub>NC</sub> <sup>[i]</sup> [%]	S <sub>CP</sub> <sup>[j]</sup> [%]
1	С	/	0.18	240	58	37	63	30	24	3	22	13
2	H-ZSM-5	140	1.54	15	68	20	29	3	11	0	17	53
3	Na-ZSM-5	140	0.32	240	74	35	48	6	19	3	17	32
4	Cs-ZSM-5	140	0.16	240	54	27	49	11	18	2	25	25
5	H-BETA	180	1.74	15	77	36	47	5	17	2	24	27
6	Cs-BETA	180	0.57	60	69	46	67	13	36	2	21	10
7	H-Y	2.5	2.27	15	100	0	0	0	0	0	0	100
8	Na-Y	2.5	2.27	15	100	0	0	0	0	0	0	100
9	H-USY	15	2.27	15	100	0	0	0	0	0	0	100
10	Na-USY	15	2.27	15	100	0	0	0	0	0	0	100
11	H-USY	30	2.27	15	100	0	0	0	0	0	0	100
12	H-USY	40	1.29	30	73	33	45	4	16	12	30	13
13	Na-USY	40	0.95	30	74	46	62	7	23	2	14	22
14	Cs-USY	40	0.86	30	82	67	82	10	31	1	9	9

[a] Reaction conditions:  $T = 165 \,^{\circ}$ C, [ML] = 7 mmolL<sup>-1</sup>, 0.8 g 0.5 Ru/zeolite or 0.08 g 5 Ru/C, Ru/ML = 4 wt%, pretreatment of the catalysts in nitrogen at 350  $^{\circ}$ C (Table 3, entry 2). [b] Initial activity (after 15 min). [c] Conversion of ML. [d] Yield of CLA. [e] Selectivity for total CLA. [f] Selectivity for *cis*-9,*trans*-11-+*trans*-10,*cis*-12-CLA. [g] Selectivity for *trans*-9,*trans*-11-+*trans*-10,*trans*-12-CLA. [h] Selectivity for hydrogenation products (C18:1+C18:0). [j] Selectivity for non-conjugated C18:2 isomers. [j] Selectivity for catalyst-adsorbed material (coke) (deficiency of carbon mass balance).

non-conjugated C18:2 isomers (NC), hydrogenated products (HP) and coke (CP), which remains on the catalyst and thus is detected as a deficiency in the carbon mass balance. An overall reaction network for linoleic acid disappearance is shown in Scheme 1. The formation of conjugated and non-conjugated C18:2 isomers is equilibrium limited, whereas the formation of hydrogenated products and coke is irreversible. The selectivity for the different product classes, as well as for the beneficial CLA isomers, namely, *cis*-9,*trans*-11-+*trans*-10,*cis*-12-CLA ( $S_{ct}$ ), and *trans*-9,*trans*-11-+*trans*-10,*cis*-12-CLA ( $S_{ct}$ ), at comparable conversions is given in Table 2 for all catalysts.

It seems that the type of support has a large influence on both methyl linoleate conversion and CLA selectivity. Zeolites Y and USY, with a Si/Al ratio of  $\leq$  30, do not show any CLA formation, irrespective of the countercation present in the zeolite lattice (Table 2, entries 7-11). In all cases the conversion is very high, since after reaction for 15 min all methyl linoleate has disappeared. The products, collectively denoted as hydrocarbon coke (CP), remain strongly adsorbed on the catalyst surface. Reaction simulation in a thermobalance indicated that all reactant remained adsorbed on the catalyst support. These observations can be explained by the high acid density of such zeolites. It is known that olefins can undergo proton-catalysed reactions on acid sites, such as isomerisation, polymerisation and cyclisation,  $\overset{\scriptscriptstyle [13]}{,}$  polymerisation products are trapped in the pore system of the support. Furthermore, it has already been shown that CLAs can also polymerise on Ru catalysts.<sup>[12a, 14]</sup> Also Na-exchanged Y and USY zeolites with low Si/Al ratios show coke formation (Table 2, entries 8 and 10), caused by protons produced during the reduction of ion-exchanged Ru<sup>III</sup>-hexamine. Thus, zeolites with a low Si/Al ratio ( $\leq$  30) are not suitable supports for the formation of CLAs because of their high activity for coke formation.

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In contrast, with Ru/USY catalysts with a Si/Al ratio of 40, large quantities of CLAs were identified in the reaction mixture (Table 2, entries 12–14). Furthermore, the activity of these catalysts was much higher than that of the Ru/C reference catalyst, namely,  $1.29 \times 10^{-5}$  and  $0.18 \times 10^{-5}$  molmin<sup>-1</sup> for Ru/H-USY(40) and Ru/C, respectively.

Also, zeolite topology has an influence on the reaction characteristics. A comparison of Ru/H-ZSM-5, Ru/H-BETA and Ru/H-USY(40) revealed that, at comparable conversions, zeolite BETA (with small crystallites) and USY (with mesopores) show a higher selectivity for CLA formation (29, 47, and 45%, respectively; Table 2, entries 2, 5 and 12). It should be stressed that the

small pores of ZSM-5 show a higher reactivity for coke formation. Probably the reactive conjugated products either undergo slow intraporous polymerisation or just block these pores.

On the three catalysts, the nature of the products is the same, though the individual selectivities are different. Among the BETA and USY topology, the individual CLA selectivity is comparable, indicating that, for the more open zeolite lattices, pore architecture is not a selectivity-dominating parameter. It is important to note that in earlier work, dealing with the differentiation between *trans*- and *cis*-fatty acids, a clear influence of the same zeolite topologies for the selective removal of *trans*-fatty acids from a mixture containing both *cis* and *trans* isomers has been reported.<sup>[15]</sup>

The use of different countercations (H<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup>) in the ZSM-5 support has a large influence on the activity (Table 2, entries 2-4); the activities of Ru/Cs-ZSM-5 and Ru/Na-ZSM-5 are reduced compared with Ru/H-ZSM-5. Ru/Cs-ZSM-5 shows the lowest activity, which is comparable with that of Ru/C. Because the presence of bulky Cs<sup>+</sup> ions, rather than the nature of the charge compensating cations, namely, Na<sup>+</sup> and Cs<sup>+</sup>, affect overall catalyst behaviour, it seems that pore blocking in ZSM-5 with larger cations could be at the basis of reduced activity. An effect of the nature of the charge-compensating cations is also encountered with BETA (Table 2, entries 5 and 6) and USY(40) samples (Table 2, entries 12-14), mainly at the level of the CLA selectivity. More basic Cs catalysts show an enhanced selectivity for CLA formation, whereas acid catalysts show enhanced activity for the formation of coke  $(H^+ > Na^+ > Cs^+)$ . Larger monovalent cations in zeolites result in reduced electronegativity of the material,<sup>[16]</sup> and according to Sanderson, reduced acid strength of the residual Brønsted acid sites.<sup>[17]</sup> This explains the reduced selectivity for coke and non-conjugated isomers of ML; the latter is obtained by acid-catalysed isomerisation. The enhanced CLA yield and selectivity should be attributed to changes in the properties of the Ru metal clusters under the influence of the enhanced basicity of the lattice. It is expected that these changes occur at the level of the residual electron density on the clusters. How this mechanistically affects CLA formation will be discussed below. The highest CLA selectivity is obtained with the Ru/Cs-USY(40) catalyst, namely, 82% at a conversion of 82% (Table 2, entry 14), which is much higher than that of the Ru/C catalyst, namely, 63% at a conversion of 58% (Table 2, entry 1). Ru/C shows a higher selectivity towards cis-9, trans-11- and trans-10, cis-12-CLA isomers, whereas Ru/Cs-USY is more selective towards the formation of trans,trans-CLAs. This issue will be further discussed below.

It is important to mention that Ru/Cs-USY shows very low selectivity for hydrogenated products due to the absence of a hydrogen donor. In the presence of molecular hydrogen<sup>[12d-f]</sup> or after pre-activation under hydrogen,<sup>[12b]</sup> higher selectivities for hydrogenated products have invariably been reported.

### Determination of active sites

From the above experiments it follows that superior CLA production occurred with the Ru/Cs-USY(40) catalyst. NMR spectroscopy measurements of the solvent, namely, n-decane, after the reaction, revealed that the solvent was inert under the reaction conditions. To identify the active centres responsible for the isomerisation reaction, tests were performed by using Cs-USY(40) devoid of Ru. After reaction for 1 h, a CLA yield of only 1 wt% and a conversion of 5 wt% was obtained, compared with a CLA yield of 75 wt% and a conversion of 94 wt% for added Ru (Table 3, entries 1 and 2). Hence, the ML isomerisation activity towards CLAs can be assigned to the presence of Ru. If no Ru is present, 3 wt% of coke is formed after 1 h, whereas 5 wt% of coke is formed with the Ru/Cs-USY catalyst. In agreement with the literature, this indicates that not only the support, but also Ru contributes to the formation of coke.<sup>[12a, 14]</sup> However, it cannot be excluded that the higher amount of coke for Ru/Cs-USY might also be associated with the higher activity of this catalyst with respect to ML isomerisation to CLA.

<b>Table 3.</b> Isomerisation of ML with various USY(40) catalysts, using different activation procedures. <sup>[a]</sup>								
Entry	Catalyst	Activation	X <sub>ML</sub>	$Y_{\rm CLA}$	Y <sub>NC</sub>	$Y_{\rm HP}$	$Y_{\rm CP}$	
1	Cs/USY	$N_2/H_2/air^{[b]}$	5	1	0	0	3	
2	Ru/Cs-USY	$N_2/H_2/air^{[b]}$	94	75	10	2	5	
3	Ru/Cs-USY	N <sub>2</sub> /air	83	55	19	3	5	
4	Ru/Cs-USY	$N_2/O_2/air^{[c]}$	85	57	15	2	9	

4	Ru/Cs-USY	$N_2/O_2/air^{[c]}$	85	57	15	2	9
5	Ru/Cs-USY	$N_2/H_2^{[d]}$	100	55	20	7	15
[a] Read 60 min; N <sub>2</sub> and ture tra 350°C, [d] Tran inert co	tion conditions abbreviations $H_2$ up to 350 and ansfer from a fi followed by sfer of the redunditions.	5: 165°C, [ML are the same nd 400°C, resp low to a batc room-tempera uced catalyst f	]=7 mm as those pectively, h reacto ature cou rom a flo	ol L <sup>-1</sup> , given followe r in air ntact v ow to a	0.8 g 0. in Table ed by roo . [c] Unc vith a batch r	5 Ru/US e 2. [b] om-ten ler N <sub>2</sub> flow c eactor	SY(40), Under npera- up to of O <sub>2</sub> . under

In a next step, the Ru dispersion was determined by CO chemisorption, TEM analysis and extended X-ray absorption fine-structure (EXAFS) measurements. Ru dispersion from CO chemisorption was very high, namely, 87%, which indicated the presence of highly dispersed Ru. With TEM, no Ru clusters could be detected, whereas EDX measurements at different points on the zeolite confirmed the presence of Ru, implying that Ru was indeed highly dispersed throughout the zeolite crystal.

While ML isomerisation activity of such highly dispersed Ru was not known, its existence has been described before.<sup>[18]</sup> From the literature, it is known that activation conditions are crucial to arrive at such high Ru dispersions.<sup>[18a, 19]</sup> As described in the Experimental Section, [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>-exchanged zeolite was first heated under N<sub>2</sub> to 350 °C. MS analysis of the decomposition gases revealed loss of H<sub>2</sub>O (from room temperature to 150  $^{\circ}$ C) and NH<sub>3</sub> (from 220 to 350  $^{\circ}$ C), corresponding to zeolite dehydration and decomposition of the Ru complex. In a further step, the catalyst was reduced under a flow of H<sub>2</sub> at 400 °C (5 °C min<sup>-1</sup>). Almost no hydrogen was consumed, in agreement with previous work using a Ru/Na-Y(2.4) catalyst.<sup>[18a]</sup> Experimentally, it was confirmed that by omitting the reduction step, high conversions were also obtained, although the CLA yield decreased from 75 to 55 wt% (Table 3, entries 2 and 3). Hence, no hydrogen was required when highly dispersed Ru/USY catalysts were used for the production of CLA, or in the pre-treatment procedure of the catalyst or during the isomerisation reaction.

From a previous report it is known that highly dispersed nano-sized metallic Ru clusters in zeolite Y, are easily oxidised at room temperature.<sup>[18a]</sup> This was confirmed with the Ru/Cs-USY catalyst by means of an O2 titration experiment at room temperature, immediately after the activation procedure, without making contact with air. The high uptake of O<sub>2</sub> at room temperature (with  $Ru/O = \approx 2$ ) proved that metallic Ru was rapidly converted to RuO<sub>2</sub>, in agreement with the literature. EXAFS measurements also confirm the presence of Ru<sup>4+</sup> species, which are structurally similar to RuO<sub>2</sub> species.<sup>[20]</sup> The ruthenium K-edge X-ray absorption near-edge structure (XANES) spectrum of Ru/Cs-USY(40) is compared with anhydrous RuO<sub>2</sub>, as well as (hydrated) RuCl<sub>3</sub>, in Figure 1. The ruthenium K-edge energies and the detailed XANES features of the sample are very similar to that of anhydrous ruthenium oxide, but significantly different from ruthenium chloride, indicating a very similar local geometry and similar electronic properties between the sample and anhydrous RuO<sub>2</sub>. This indicates that the ruthenium metal clusters in the catalyst after reduction are oxidised to Ru4+, due to contact with air/oxygen at room temperature. Fourier transform (FT) of the EXAFS data (Figure 2) confirms the structural similarities between the anhydrous RuO<sub>2</sub> and the Ru/Cs-USY(40) sample. A similar radial distribution of the same neighbours is observed, albeit at longer distances (from  $\approx$  3.0 Å) significantly fewer contributions are observed for the catalyst sample. EXAFS analysis suggests octahedral coordination of O around Ru with two Ru-O bonds with distances of 2.01 Å, four Ru-O bonds with distances of 1.95 Å and one Ru-Ru bond with a Ru-Ru distance of 3.16 Å. Where-



**Figure 1.** Ruthenium K-edge XANES spectra for samples of anhydrous ruthenium oxide (-----), ruthenium chloride (-----) and the catalyst 0.5 Ru/Cs-USY(40) (----).



**Figure 2.** Radial distribution function from the FT of the k2-weighted EXAFS for ruthenium oxide (anhydrous) (\_\_\_\_\_), ruthenium chloride (hydrate) (-----) and 0.5 Ru/Cs-USY(40) (\_\_\_\_\_).

as in the RuO<sub>2</sub> references, further RuO and RuRu contributions can be fitted at around 3.4 and 3.5 Å, these cannot be determined for the Ru catalyst sample because no significant higher contributions are present for this sample. This indicates that significantly smaller ruthenium oxide entities are present in the catalyst sample, which would also explain the slight decrease in white-line features and small-edge energy shifts. Other authors also observed nano-sized RuO<sub>2</sub> species in FAU-type zeolites.<sup>[21]</sup> In this research, the RuO<sub>2</sub> clusters showed a two-dimensional structure of independent chains, in which RuO<sub>6</sub> octahedra were connected through two shared oxygen atoms. This is also a possible explanation for our EXAFS data.

The results of the ML isomerisation reaction with a Ru/Cs-USY(40) catalyst, which was in contact with an  $O_2$  flow (2 mL s<sup>-1</sup> g<sup>-1</sup>) for 60 min at room temperature (Table 3, entry 4), shows no activity nor selectivity differences with a catalyst that did not receive such a treatment (Table 3, entry 3). Therefore, in both cases there should be the presence of highly dispersed RuO<sub>2</sub>, at least at the moment the catalyst is added to the batch reactor. If the catalyst was not in contact with air before the reaction, and hence the Ru species were fully reduced before reaction, high activity for ML conversion was observed (Table 3, entry 5) with a somewhat higher selectivity for hydro-

genated and non-conjugated C18:2 isomers. Indeed, with this catalyst, more hydrogen was available on the catalyst surface, leading to enhanced consecutive isomerisation and hydrogenation.

If isomerisation is performed under a hydrogen atmosphere or if the catalyst is previously pre-activated under hydrogen, the metallic sites on the catalyst will be covered with chemisorbed hydrogen. In this case, the double-bond migration reaction can be rationalised by the generally accepted Horiuti-Polanyi mechanism, in which a hydrogen atom derived from a hydrogen-chemisorbed site is added to chemisorbed linoleic acid, resulting in a chemisorbed half-hydrogenated intermediate.<sup>[22]</sup> If hydrogen is absent and RuO<sub>2</sub> species instead of Ru<sup>0</sup> clusters are present, the conjugation needs to be explained by another mechanism. It has already been suggested that ruthenium at its highest oxidation state favours double-bond isomerisation.<sup>[14b]</sup> On (basic) metal oxide a possible reaction mechanism consists of the occurrence of a U-form carbanion intermediate and an allylic mechanism.<sup>[23]</sup> In basic conditions a large amount of cis, cis product indicates a high degree of stereospecificity, in line with the nature of the proposed intermediate carbanion. Alternatively, carbenium ions can be formed with the assistance of Brønsted acid sites,<sup>[24]</sup> requiring initial cis/trans product ratios of around one. This is clearly not the case because cis-cis conjugated CLA is only present in trace amounts (see below).

Because in our system no chemisorbed hydrogen atoms are present on the catalyst before reaction, they should originate from the solvent or the ML substrate. Preliminary results using a pure mixture of fatty acid esters demonstrate that no solvent is needed to conduct the isomerisation. Hence, it can be concluded that the substrate must take part in the hydride-transfer reaction to generate chemisorbed hydrogen atoms on the Ru surfaces. This has also been suggested previously.<sup>[14b]</sup>

#### Influence of catalyst activation conditions

From the above results, it follows that a nitrogen-activated Ru/ Cs-USY catalyst is oxygen sensitive. Although a somewhat lower activity is obtained, the formation of RuO<sub>2</sub> species on the catalyst has a positive influence on the CLA yield. In contrast, analysis of the literature leads to the conclusion that the formation of RuO<sub>2</sub> species during the decomposition step, by using  $O_2$  instead of  $N_2$ , greatly influences the Ru dispersion, since upon reduction large Ru clusters are formed on the external surface of the zeolite.<sup>[18a, 19c]</sup> Indeed, TEM images clearly show the presence of large Ru clusters on the external crystal surface of the O<sub>2</sub>-pretreated catalyst (up to 20–200 nm) (Figure 3). In contrast to the N<sub>2</sub>-activated sample, these clusters contain only metallic Ru because no oxygen was detected by EDX measurements. The Ru dispersion, calculated from CO chemisorption measurements, of the O2-activated sample (after reduction) is only 4%, whereas the N<sub>2</sub>-pretreated sample has a Ru dispersion of 87%. The performance of both catalysts in the ML isomerisation reaction is compared at similar conversions in Table 4. Not only is the N2-pretreated catalyst much more active, but also shows a much higher selectivity for CLA

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**Figure 3.** a) A bright-field TEM image of a large cluster in the O<sub>2</sub>-activated Ru/Cs-USY(40) catalyst. b) A high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the same large cluster (bright white). c) A colour map showing that the large cluster is metallic ruthenium, not ruthenium oxide. d)–g) STEM electron energy-loss spectroscopy (EELS) elemental maps for C (d), O (e), Ru (f) and Si (g) obtained from the region indicated in the HAADF-STEM image, e)–g) are combined into the colour map in c).

formation, whereas the  $O_2$ -pretreated catalyst has a higher selectivity towards non-conjugated C18:2 isomers (NC) and coke (CP). Hence, it seems clear that small Ru oxide species, obtained after pre-treatment in an inert atmosphere followed by room-temperature exposure to air, should be the active sites for CLAs formation. Larger Ru metal clusters obtained after oxygen activation and subsequent reduction are not sensitive to room-temperature air contact and should lead to higher levels of undesired non-conjugated C18:2 isomers.

Interestingly, the Ru cluster size also has an influence on the CLA isomer distribution. Smaller Ru(oxide) clusters (decomposition under N<sub>2</sub>) show an enhanced selectivity for the formation of *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers compared with the larger Ru clusters (decomposition under O<sub>2</sub>). With the N<sub>2</sub>-activated catalyst, the *cis*-9,*trans*-11 and *trans*-10,*cis*-12 isomers are initially the dominantly formed CLA isomers. After longer reaction times, the latter isomers are mainly converted

to the thermodynamically more stable *trans*-9,*trans*-11- and *trans*-10,*trans*-12-CLA isomers, whereas only minimal positional isomerisation is observed after 6 h of reaction. With the O<sub>2</sub>-activated catalyst, both the *cis*-9,*trans*-11-+*trans*-10,*cis*-12- and *trans*-9,*trans*-11-+*trans*-10,*trans*-12-CLA levels decrease after longer reaction times. Simultaneously, the concentration of other positional CLA isomers increases.

However, it should be stressed that the physicochemically identified highly dispersed Ru oxide species are not necessarily present under ML isomerisation conditions (around 165 °C). Indeed, it is known that such species are easily reduced to small metal clusters after hydrogen treatment at around  $100 \,^\circ C$ .<sup>[18a]</sup> Moreover, it is conceivable that upon contact with ML at reaction temperature, ML is oxidised by the highly reactive RuO<sub>2</sub>, at the same time, probably reducing Ru to the metallic state. It is known that weakly bonded oxygen species exist in RuO<sub>2</sub>. The oxygen atoms are easily transferred to CO or alcohol even at room temperature, thereby reducing Ru into small clusters.<sup>[21,25]</sup>

In conclusion, it is not necessary to invoke the presence of  $RuO_2$  clusters for CLA formation and the occurrence of a carbanion mechanism. The reduction to Ru metal clusters by initial ML autoxidation reaction conditions and the occurrence of a common Horiutu–Polanyi mechanism is straightforward. The favourable effect of small Ru metal particle sizes for CLA selectivity is clear.

#### Influence of ML concentration

The influence of ML concentration on the reaction characteristics of ML isomerisation with a Ru/Cs-USY(40) catalyst was investigated. Indeed, to obtain a process with a high productivity and TOF, and hence, to make the process industrially attractive and sustainable, it is important that the catalyst is able to convert ML into CLAs in a reaction with a low Ru/ML ratio with a high selectivity and activity. In Table 5 the activity and different selectivities towards the formation of CLAs, non-conjugated C18:2 isomers, hydrogenated products and cokes at maximum CLA yield are compared (entries 1-4). It is shown that the activity rises as the ML concentration is increased from 7 to 350 mmol L<sup>-1</sup>. This leads to a very significant increase in productivity and TOF; the productivity at maximum CLA yield increases from 0.029 to 0.391 g(CLA)  $L^{-1}\,\text{min}^{-1}$  and the TOF increases from 8.1 to 99.8 h<sup>-1</sup>. At somewhat lower CLA yields, namely, 67 instead of 75 wt%, the productivity and TOF are even higher, namely, 0.698 g(CLA) $L^{-1}$ min<sup>-1</sup> and 175.5 h<sup>-1</sup>, re-

Table 4. Performance of a N <sub>2</sub> - and O <sub>2</sub> -pretreated Ru/Cs-USY(40) catalyst in the isomerisation of ML. <sup>[a]</sup>											
Activation	D <sub>Ru</sub> <sup>[b]</sup>	$A_{i}^{[c]} \times 10^{-5}$	t	Х <sub>мL</sub>	Y <sub>CLA</sub>	S <sub>cla</sub>	S <sub>ct</sub>	S <sub>tt</sub>	S <sub>NC</sub>	S <sub>нР</sub>	S <sub>сР</sub>
	[%]	[mol min <sup>-1</sup> ]	[min]	[%]	[wt%]	[%]	[%]	[%]	[%]	[%]	[%]
$N_2/H_2/air^{[d]}$	87	19.24	120	82	67	82	44	30	6	1	11
$O_2/H_2/air$	4	3.40	480	83	19	23	3	11	35	2	39
[a] Reaction conditions: $T = 165 ^{\circ}$ C, [ML] = 350 mmol L <sup>-1</sup> , 0.8 g 0.5Ru/Cs-USY(40), abbreviations see Table 1. [b] Ru metal dispersion from CO measurements for in situ pretreated samples. [c] Activity after reaction for 15 min. [d] Same conditions as Table 3, entry 2.											

spectively (Table 1, entry 13). These values are much higher than those of other heterogeneous processes found in the literature and are comparable to the homogeneous process used industrially today (Table 1). Only Ru/C shows a slightly higher productivity when using technicalgrade linoleic acid in undiluted conditions (Table 1, entry 6).

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 Table 5. Influence of the ML concentration on the performance of the Ru/USY(40) catalyst in the isomerisation of ML.<sup>[a]</sup> Results are given for maximal CLA yield.

Entry	Counter cation	[ML] [mmol L <sup>-1</sup> ]	$A_i \times 10^{-5}$ [mol min <sup>-1</sup> ]	Х <sub>мL</sub> [%]	t [min]	Y <sub>CLA</sub> [wt%]	P [g(CLA) L <sup>-1</sup> min <sup>-1</sup> ]	TOF <sup>(t</sup> [h <sup>-1</sup> ]
1	Cs	7	0.86	94	60	69	0.029	8.1
2	Cs	21	2.85	92	60	74	0.093	23.7
3	Cs	70	12.25	92	60	77	0.289	78.9
4	Cs	350	19.24	93	240	75	0.391	99.8
5	Н	7	1.29	73	30	33	0.028	12.5
6	н	350	14.72	81	360	40	0.139	57.9
7	Na	7	0.95	93	60	47	0.020	8.0
8	Na	350	11.32	81	360	68	0.236	57.9

However, much more Ru is required to obtain such high productivity. The TOF for Ru/Cs-USY is indeed one order of magnitude larger than that of Ru/C.

The selectivity for the different products (CLA, non-conjugated CLA, hydrogenated products and coke) remains rather unaffected by ML concentration. In contrast, the CLA isomer distribution as a function of the conversion is largely influenced by the Ru/ML ratio (Figure 4). Initially, the contribution of the cis-9,trans-11 and trans-10,cis-12 isomers is high and at high ML conversion levels off at around 10%. The contribution of these beneficial isomers among all CLAs increases with higher ML levels. Also, the fraction of the trans-9, trans-11- and trans-10,trans-12-CLA isomers shows the same behaviour when plotted against conversion. Its contribution indicates values around 35% for higher ML levels. It is clear, at least for the high ML concentrations, that cis, trans (trans, cis) isomers are the primary CLA product isomers, followed by consecutive formation of trans, trans and unconjugated CLAs. For lower initial ML concentrations, the equilibrium is reached at lower ML conversion. The data allow the 9,11- and 10,12-CLA product distribution to be determined at equilibrium: cis,trans 27.5, trans,trans 65.5 and cis, cis 7%. The level of other positional CLA isomers increases with conversion and is higher for lower ML concentrations. At equilibrium around 45% of the total CLA isomers are present as CLAs with double bonds on positions different from 9,11 and 10,12.

From these observations it can be concluded that the initially kinetically formed *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers are converted to the thermodynamically more stable *trans*-9,*trans*-11- and *trans*-10,*trans*-12-CLA isomers and the 9,11 and 10,12 isomers are converted to other positional CLAs for longer reaction times. Both phenomena are enhanced for reduced ML concentration.

### Influence of the nature of the counterion in Ru/R-USY(40)

Owing to the positive influence of a low Ru/ML ratio on the reaction characteristics, Ru/R-USY catalysts, with R=Me, H, Na, or Cs, were tested in the isomerisation of a more concentrated solution of ML, namely,  $[ML]=350 \text{ mmol L}^{-1}$ . With each catalyst, much higher productivities, specific yields and selectivities towards the desirable CLA isomers were obtained compared with the respective reactions with a low ML concentration (7 mmol L<sup>-1</sup>). Comparison of the three catalysts at [ML] =350 mmol L<sup>-1</sup>, shows that the Ru/Cs-USY catalyst gives the highest CLA yield, and hence, also the highest productivity and TOF (Table 5, entries 4, 6 and 8). The obtained TOFs are considerably higher than those calculated from the literature (Table 1).



**Figure 4.** Influence of the Ru/ML ratio on the CLA isomer product distribution (PD) during the isomerisation of methyl linoleate using a Ru/Cs-USY(40) catalyst: A) PD<sub>ct</sub> (*cis*-9,*trans*-11+*trans*-10,*cis*-12-CLA), B) PD<sub>tt</sub> (*trans*-9,*trans*-11+*trans*-10,*trans*-12-CLA), C) PD<sub>other CLA</sub> (other positional CLA isomers); [ML] = 7 ( $\blacktriangle$ ), 21 ( $\blacksquare$ ), 70 ( $\bigcirc$ ) and 350 mmol L<sup>-1</sup> ( $\diamond$ ).

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Furthermore the Ru/Cs-USY catalyst shows the highest selectivity for desirable *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers (Figure 5). With the acid Ru/H-USY catalyst, faster isomerisation towards the thermodynamically more stable *trans*,*trans*-CLAs takes place, as well as positional isomerisation of the 9,11 and 10,12 isomers to both conjugated and non-conjugated C18:2 isomers. The more basic Na- and Cs-exchanged USY catalysts show a much lower initial activity for formation of *trans*-9,*trans*-11- and *trans*-10,*trans*-12-CLA isomers and other positional CLA isomers. Only at higher conversions (around 50% for Ru/Na-USY and around 70% for Ru/Cs-USY), are the *cis*-9,*trans*-11- and *trans*-10,*cis*-12-CLA isomers converted to their respective geometrical *trans*,*trans* isomers and other positional CLA isomers. The level of non-conjugated C18:2 isomers only slightly increases with conversion.

The reduced rate at which CLA equilibration is reached is in line with the presence of more voluminous pore-blocking agents, namely, Na<sup>+</sup> and mainly Cs<sup>+</sup> ions. The phenomenon could therefore reflect an increased contribution of intracrystal-line diffusion limitation. The enhanced TOF for CLAs with Ru/R-USY(40) in the sequence R = Cs > Na > H, which can be derived from Table 5, indicates the occurrence of a catalyst effect promoting, in particular, the desired reaction, that is, the rate of *cis,trans*-CLA isomer formation at positions 9,11 and 10,12. It is not clear at this stage how enhanced basicity of the zeolite framework, and consequently, enhanced electron density on

the Ru metal clusters (see above) is effecting this. It is known for Pt clusters in zeolite that they receive Ir-like character (decrease in cluster electron density and faster hydrogenation/de-hydrogenation) when embedded in a more acidic Y zeolite.<sup>[26]</sup> In the present case, the opposite is clearly the case and decrease in metal-catalysed isomerisation is not unexpected. In parallel, there is a reduction in the rate at which the CLA equilibrium is reached, yielding an enhanced selectivity for *cis,trans*-conjugated CLAs.

#### **Catalyst regeneration**

Finally, the optimal Ru/Cs-USY(40) catalyst was tested in a recycling experiment. After the first run, the catalyst was filtered and washed with dioxane. After drying overnight at room temperature, the catalyst was directly tested in a second run, without any further pre-treatment. In the same way, a third run was also performed. The conversion and CLA yield of the three runs are compared in Figure 6. It can be concluded that, although there is some loss in activity, probably caused by loss of active sites as a result of coke formation, the Ru/Cs-USY catalyst remains very selective in the isomerisation of ML. Further work is in progress to deal with this coke issue and catalyst deactivation.



Figure 5. Influence of the countercation on the yield of conjugated and non-conjugated C18:2 isomers during the isomerisation of ML with Ru/H-USY(40) ( $\blacktriangle$ ), Ru/Na-USY(40) ( $\blacksquare$ ) or Ru/Cs-USY(40) ( $\blacklozenge$ ). Reaction conditions: 165 °C, [ML] = 350 mmol L<sup>-1</sup>.



**Figure 6.** Recycling experiment with Ru/Cs-USY(40) recorded after reaction for 300 min (gray = conversion of ML(350 mmol L<sup>-1</sup>), white = yield of CLA, stripes = selectivity towards CLA).

### Conclusions

The results presented clearly show that, compared with other heterogeneous processes reported in the literature, high productivities of and selectivities for CLA from ML can be obtained by heterogeneous catalysis when highly dispersed RuO<sub>2</sub> species are present in Si-rich USY catalysts, at least when added to the batch reactor. When the reactions are performed under an inert atmosphere, almost no hydrogenated products are formed, whereas conjugation seems to be performed by means of hydrogen transfer between the fatty acids and the active Ru metal clusters on the catalyst, that is, according to a classical Horiuti-Polanyi mechanism, since cis, trans-CLAs at positions 9,11 and 10,12 were shown to be primary products converted consecutively into trans, trans isomers with double bonds at the same and finally other positions. Unwanted side reactions are coke formation and formation of hydrogenated products. The latter increase in selectivity when enhanced amounts of activated hydrogen are present due to presence of hydrogen during activation or reaction. Faster equilibration among the CLAs is obtained when the size of the charge-compensating cations is reduced ( $Cs^+ > Na^+ > H^+$ ). This can be the result either of enhanced intracrystalline diffusional resistance or of enhanced activity of Ru metal clusters in a more basic catalyst support.

Though in physicochemical terms the presence of highly Ru oxide clusters was clearly demonstrated on the reduced catalyst exposed to air at room temperature, it was assumed that such clusters in reaction conditions were transformed into highly dispersed Ru metal clusters through the autoxidation of ML by Ru–O.

Because of the very high productivities obtained with the Ru/Cs-USY(40) catalyst, this process could be a major breakthrough in the production of bio-based drying oils, paints and plastics. Moreover, because the beneficial CLA isomers are the main products with the Ru/Cs-USY catalyst, this research may also accelerate the development of CLA-enriched functional foods.

### **Experimental Section**

### Materials

Zeolite samples were from Zeolyst (ZSM-5=CBV28014, Y=CBV100, USY=CBV720, CBV760 and CBV780, BETA=CP811C-300), whereas the commercial Ru/C catalyst was from Johnson Matthey (5 wt% Ru, Type 97). ML was from Sigma-Aldrich with a purity of >99%, *n*-decane was from Acros with a purity of >99%. CLA references for peak identification, namely, *cis*-9,*trans*-11-, *trans*-10,*cis*-12-, *trans*-9,*trans*-11-, *cis*-9,*cis*-11- and *cis*-10,*cis*-12- (C18:2) CLA, were from Matreya LLC.

### **Catalyst preparation**

The supports were loaded with 0.5 wt % Ru ion exchange for 24 h under stirring of the aqueous zeolite slurry (200 mL water per gram of dry zeolite), containing the required amount of Ru precursor ([Ru<sup>III</sup>(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>]). Afterwards, the Ru-hexamine-exchanged zeolite powder was filtered, washed with distilled water and dried overnight at 50 °C. Prior to metal loading, the zeolite powder was changed from the proton to the NH<sub>4</sub> form by adding an aqueous solution of ammonia (0.015  $\mbox{m})$  for 16 h (200  $\mbox{mLg}^{-1}\mbox{)}.$  The obtained NH<sub>4</sub> zeolite was transformed into the Na form by two successive room-temperature ion-exchange steps (16 h) with a 1 м aqueous solution of NaCl (200 mL per gram of dry zeolite). The caesium form was obtained by exchanging the sodium zeolite twice with a 0.1 м aqueous solution of caesium acetate (25 mLg<sup>-1</sup> zeolite) for 48 and 72 h. After each exchange step, the slurry was filtered, the solids were washed three times with distilled water and air-dried at 100°C.

Prior to activation, the dry powders were compressed, crushed and sieved. The 0.25–0.50 mm fraction was retained for further use. Activation was conducted in a flow reactor in two steps under a flow of nitrogen (120 mLmin<sup>-1</sup> g<sup>-1</sup>). First, the reactor was heated from RT to 200 °C at 2 °Cmin<sup>-1</sup> and then from 200 to 350 °C at 3 °Cmin<sup>-1</sup>. Optionally, a reduction step at 400 °C (5 °Cmin<sup>-1</sup>) under a flow of hydrogen (120 mLmin<sup>-1</sup> g<sup>-1</sup>) was performed. The catalyst pellets were then transferred from the flow reactor to a stirred batch reactor, requiring a short exposure to air at room temperature.

### **Catalyst characterisation**

For investigations with TEM, the sample was dispersed in ethanol and deposited on a holey carbon grid for analysis. Bright-field TEM, HAADF-STEM and STEM-EELS spectrum image mapping was carried out in a FEI Titan 80-300 "cubed" microscope equipped with a Gatan Quantum spectrometer. The convergence angle,  $a_i$ , was about 20 mrad, the collection semi-angle,  $\beta$ , was about 100 mrad. The maps were generated by integrating the background-subtracted signal from the carbon K edge, oxygen K edge, ruthenium M<sub>4,5</sub> edge and the Si K edge in each EELS spectrum. The scanned area was  $69 \times 125$  nm divided into  $61 \times 67$  pixels in the spectrum image. Ru K-edge EXAFS spectroscopy experiments were carried out at the Diamond Light Source in Didcot, UK, beamline B18 (Core XAS). A double-crystal monochromator Si(311) was used. The measurements were performed in fluorescence mode by using a nine-element Ge solid-state detector. The spectra were calibrated by using a Rh foil (1st maximum 1st derivative: 23220 eV). The samples were prepared by pressing around 50 mg of the activated catalyst pellets into tablets. These tablets were placed into a sample holder with kapton film as an X-ray transparent window. The experiments were performed at room temperature. XAS data processing and EXAFS analysis were performed by using IFEFFIT<sup>[27]</sup> with the Horae package (Athena and Artemis).<sup>[28]</sup> The crystallographic RuO<sub>2</sub> data (space group 136; a=b=4.919, c=3.1066 Å) were used as a starting fitting model.<sup>[20]</sup> Ru K-edge EXAFS fitting results (the error is the last digit in parentheses): 2RuO at 2.01(2) Å, Debye–Waller factor  $\sigma^2=0.001(1)$  Å<sup>2</sup>, 4RuO at 1.95(4) Å,  $\sigma^2=0.006(6)$  Å<sup>2</sup>, 2RuRu at 3.16(3) Å,  $\sigma^2=0.009(3)$  Å<sup>2</sup>,  $E_0=-5.1(2)$  eV, *R* factor 2.3%; fitting ranges 1.49 < *k* < 11.18 Å<sup>-1</sup>; 1.00 < *R* < 3.11 Å, 12 independent data points,  $k^2$ -weighted fit, amplitude 1.0 (fixed).

Ruthenium dispersions were determined by using CO chemisorption. Catalyst pellets loaded in a tubular reactor were activated according to the pre-treatment procedure described previously and cooled to room temperature under a flow of helium. For the titration of the Ru surface, pulses of pure CO (5 µL) at an interval of 2 min were added to a helium flow of 10 mLmin<sup>-1</sup>. The CO concentration in the outlet stream was followed continuously by ion monitoring at m/z 28 with a Pfeiffer Omnistar quadrupole mass spectrometer. For the calculation of the dispersion, adsorption of one CO per accessible Ru atom was assumed. In the same way, pulses of pure H<sub>2</sub> or O<sub>2</sub> were added to a helium flow for the H<sub>2</sub> and O<sub>2</sub> titration experiments, respectively. The concentration of H<sub>2</sub> and  $O_2$  in the outlet stream was determined by ion monitoring at m/z 2 and 32, respectively. The same setup was also used for the determination of the decomposition products during the activation of the catalysts under N<sub>2</sub>. By monitoring at m/z 16, 17 and 18, the concentrations of NH<sub>2</sub><sup>+</sup>, NH<sub>3</sub> and H<sub>2</sub>O species, respectively, were followed.

Thermogravimetric analysis (TGA) was performed on a TGA Q500 (TA Instruments) instrument, while heating the sample from RT to 700  $^\circ$ C (5  $^\circ$ Cmin<sup>-1</sup>) under oxygen.

### **Isomerisation reaction**

Isomerisation of ML at 165 °C was carried out in a 100 mL Parr autoclave with a sampling device and under 3.5 bar of N<sub>2</sub> with constant stirring (500 rpm). In a typical experiment, *n*-decane (40 g), ML (0.1–5.0 g) and 0.5 Ru–zeolite (0.8 g) catalyst (or 5 Ru/C (0.08 g)) were used.

#### Analysis methods

The fatty acid methyl esters were analysed by using a Hewlett Packard HP 6890 gas chromatograph with a split injection system (split ratio = 100:1) and N<sub>2</sub> as the carrier gas. A 100 m CP-SIL 88 highly polar capillary column with an internal diameter of 0.25 mm and a film thickness of 0.2  $\mu$ m was used for separation. Initially, the column temperature was maintained at 180 °C for 50 min and then raised at 10 °C min<sup>-1</sup> to 225 °C and held there for 15 min. The FID detector used was maintained at 280 °C. Heptadecane was used as the internal standard. Most CLA isomers were identified based on retention times, using references from Matreya LLC. Other CLA isomers were identified based on literature data<sup>[29]</sup>.

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