Synergetic effect of Ruthenium and basicity sites in Ru-MgAl catalyst for hydrogen-free production of conjugated linoleic acids

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Abstract

A series of Ru-MgAl composite oxides catalysts prepared by calcining the ruthenium grafted hydrotalcite-like precursor at various temperatures were used in the hydrogen-free production of conjugated linoleic acid. The effect of calcination temperature on textural, base and catalytic properties of the materials was investigated. Results indicated that the Ru-MgAl composite oxides calcined at 450 ^{o}C showed high activity, namely, *CLA* productivity, *CLA* production rate and TOF up to 1.52g *CLA* g (*CLA*) L^{-1}(solvent) min^{-1}, 284g (*CLA*) g^{-1}(Ru) h^{-1} and 102.6mol (*LA* converted) mol^{-1}(Ru) h^{-1}. Moreover, the biologically active *CLA* isomers, *cis-9, trans-11, trans-10, cis-12 and trans-9, trans-11-CLA*, were the main products, while almost no hydrogenated products were formed. Meanwhile, the role of ruthenium and basicity sites in the catalytic reaction was been studied. It was found that the basicity sites of Ru-MgAl catalyst and ruthenium activity site seem to have a synergic effect on the catalytic reaction. The possible reaction mechanism for the isomerization was also proposed.

Key word: composite oxides, isomerization, conjugated linoleic acid, bifunctional catalysts, hydrogen-free

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1. Introduction

Conjugated linoleic acid (*CLA*) is a collective term used to describe the mixture of positional and geometric isomers of linoleic acid with conjugated double bonds. A vast amount of literature describing the abundant health benefits of CLAs is available today [1]. They decrease the body fat quantity and increase muscle [2], possess anti-inflammatory [3], cancer-preventive effects [4], exert beneficial effects on the skeletal system [5], act as immunostimulants[6] and decrease the probability of asthma occurrence[7]. However, several studies have shown that only a small number of *CLA* isomers, namely, *cis*-9, *trans*-11-*CLA* and *trans*-10, *cis*-12-*CLA* present interesting biomedical and nutritional properties, thus demonstrating their potential application as functional foods. Specifically, the *cis-9, trans-11*-*CLA* isomer (*c9, t11*-*CLA*) has been proposed as potential anti-tumour agent whereas the *trans-10, cis-12*-*CLA* isomer (*t10, c12*-*CLA*) affects the regulation of lipids (cholesterol) and body mass [8]. Meanwhile, recent research indicates that the *trans-9, trans-11*(*t9, t11*-*CLA*) isomer also promotes good health [9]. Hence these three fatty acids are of great interest to food and health research.

Conventionally, *CLAs* can be prepared by microbial biosyntheses and isomerization of linoleic acid with alkaline as catalysts. Some microorganisems contain specific isomerase enzymes that are able to transform linoleic acid into CLAs. Unfortunately, these bacterial species can transform the CLAs into saturated products such as stearic acid. Moreover, bacteria do not synthetize the isomer *cis-9, trans-11-CLA* until the linoleic acid concentration is high, producing the inhibition of biohydrogenation [10]. Henceforth, these bacterial species cannot be utilized for the industrial production of CLAs. For basic catalysis method, the amount of the two formed isomers(*cis*-9, *trans*-11 and *trans*-10, *cis*-12-*CLA*) is almost equal(selectivity≈

50%) and the yield is quite high(over 80%)[7]. However, the use of the strong basic potassium hydroxide or sodium methoxide is not environmentally friendly. Furthermore, *CLA* in its chemical form of a free fatty acid during alkaline isomerization is easily oxidized in air [11]; other homogeneous catalysts, such as RhCl $(pph_3)_3$, [RhCl $(C_8H_{14})_2]_2$ have been tested for the isomerization of_linoleic acid, it does not cause hydrolysis of the final product and it yields highly conjugated products. But the process is not environmentally friendly and the catalyst is difficult to separate [12].

Instead, a heterogeneous catalyst would be easy to filter and reuse, environmental problem and separation difficulties can be avoided. Bernas et al. [13-16] did pioneering work on producing conjugated linoleic acid using heterogeneous catalysts, it was showed that a great variety of supported-metal catalysts were been tested for isomerization of linoleic acid. Kreich and Claus [12] also reported the synthesis of *CLAs* over Ag/SiO_2 catalyst. The catalytic results at 438K yielded selectivity values of 35% to *c9, t11-CLA* and 26% to *t10, c12-CLA* for a 69% of conversion with a 12% of selectivity to hydrogenation products. *Cardo* et al. [17] used mordenite and ZSM-5 to yieldCLA isomers by carbenium ions. However, it can be found that the hydrogen is needed for the majority of the heterogeneous catalytic process to form the half-hydrogenated intermediates, which will finally transform into CLAs. That is to say, the elevated level of hydrogen will lead to formation of unwanted hydrogenated by-products [10]. Though the production of *CLAs* by heterogeneous catalysts without hydrogen is a difficult and complicated process, it can reduce the production of unwanted by-products. Bernas et al [18] used Ru/C catalyst for the isomerization of linoleic acid without the use of H_2. Philippaerts et al [19] described the H_2-free production of *CLA* using Ru loaded zeolite catalysts with high *CLA* production rate. The main advantage of this catalyst is that no hydrogen pretreatment or addition of hydrogen donors is required and almost no hydrogenated products are formed. However, apart from the above references, there are few publications concerning the use of heterogeneous catalysts for production of *CLAs* without hydrogen. Hence, the design of a reusable heterogeneous catalyst with high activity towards the formation of the physiologically important *c9, t11-*, *t10, c12-* and *t9, t11-CLA* isomers without using hydrogen in mild atmosphere, remains a challenge. In view of this, this paper presents a study of the use of Ru-MgAl composite oxides for production of conjugated linoleic acids in the absence of hydrogen. While almost no hydrogenated by-products are formed, high productivity of and selectivity for beneficial CALs is achieved. The role of catalyst basicities and ruthenium for the isomerization was also discussed. As know as we could, there is not dates' were found for the utilization of Ru-MgAl composite oxides catalyst for obtaining beneficial *CLAs*

2. Experimental

2.1 Materials.

Linoleic acid and methyl linoleate of 95% purity was purchased from Aladdin Reagent Co. (China). Three standard *CLA* methyl ester (*CLAME*) isomers [c9, t11; t10, c12 and t9, t11] and methyl heptadecanoate were purchased from Nu-ChekPrep.INC and kept at -20^{o}C. Various chemicals including $MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, NaOH, Na_2CO_3, $BF_3 \cdot 2CH_3OH$, $RuCl_3$, undecane were all purchased from Aladdin Reagent Co. (China). All chemicals were used as purchased without further purification.

2.2 Catalyst Synthesis

Ruthenium grafted hydrotalcites were synthesized by the hydrothermal method [20]. In a typical synthesis procedure, an aqueous solution(A) containing $MgCl_2 \cdot 6H_2O$(90mmol), $AlCl_3 \cdot 6H_2O$(20mmol) and $RuCl_3 \cdot xH_2O$(0.83mmol) in 100mL double distilled deionized water was prepared. The solution A was added dropwise into a second solution (B) containing Na_2CO_3 (130mmol) in 100 mL double distilled deionized water, in around 45min under room temperature. The mixture was maintained by adding NaOH solution to keep a constant pH of 10. Content was transferred into the Teflon coated stainless steel autoclave and aged at 80^{o}C for 16h under autogenous water vapor pressure. After 16h, the precipitate formed was filtered and washed thoroughly with hot distilled water until the filtrate was free from Cl^- ions as test by silver nitrate solution. The obtained filter cake was dried in an oven at 80 °C for 14h. The solid material named as Ru-HT. For the comparison, the sample labeled as HT was also synthesized as per the above-mentioned procedure without adding $RuCl_3 \cdot xH_2O$ or $MgCl_2 \cdot 6H_2O$. These samples were formed by calcination in air at different temperature for 4h with a heating rate of 10 °C /min. The XRF analysis results showed that the Ru-content of the catalyst was 0.8wt%, which was very similar to the ratio in the coprecipitation solution. Consequently, the catalysts were named as Ru-MgAlt, MgAlt or Ru-Alt, where t stands for calcination temperature.

2.3 Characterization of catalysts

Powder X-ray diffraction (XRD) patterns of synthesized catalysts were recorded on a Philips X'Pert MPD system equipped with XRK 900 reaction chamber, using Ni-filtered Cu Kα radiation (λ = 1.54056 Å) over a 2θ range of 5–80°. Operating voltage and current were kept at 40 kV and 40 mA, respectively. The identification of crystalline phases was made by matching the JCPDS files. Fourier transform infra-red (FT-IR) spectra of synthesized catalysts were recorded with a PerkinElmer Spectrum GX FT-IR spectrometer in the region of 400–4000cm^{-1} using KBr pellets. X-ray fluorescence analyses (XRF) were carried out with the use of an Axios mAX 4 kW, PANalytical. N_2 adsorption-desorption isotherm at -196°C was obtained using an TriStar 3000 model of gas adsorption analyzer from Micromeritics, Inc. Prior to N_2 adsorption, the samples were previously out gassed at 300 °C for 8h. BET specific areas were calculated from these isotherms using the BET method. Evolved gases analysis of the precursor decomposition was performed by mass spectrometry (EGA-MS) [21]. Samples (20mg) were placed in a U-shaped quartz reactor incorporated within a flow system, after pretreating at 100°C for 1h under a He flow of 50mL/min, then the sample was heated to 800 °C at 10 °C/min, under He flow of 50ml/min. Exhaust gases were inducted into the mass spectrometer(Hiden HPR20), the mass fragments of

OH(m/z=17) and CO_2(m/z=44) were recorded as a function of the pyrolysis temperature.CO_2-TPD studies of the samples were performed using a TPR/TPD Micromeritics ASAP 2920 instrument equipped with a thermal conductivity detector (TCD). Samples (100mg) were pretreated under a helium stream at 450 ^{o}C for 4h (10 ^{o}C/min, 50mL/min). Then, temperature was decreased until 70 ^{o}C, and a flow of pure CO_2 (50 mL/min) was subsequently introduced into the reactor during 1h. The CO_2-TPD was carried out between 70-750 ^{o}C under a helium flow (10^{o}C/min, 30mL/min).H_2-TPR studies of the samples were performed using a TPR/TPD Micromeritics ASAP 2920 instrument equipped with a thermal conductivity detector (TCD). Before reduction, the sample (around 50mg) was dried under helium flow at 120 ^{o}C for 4h. TPR was carried out between room temperature and 750 ^{o}C at a heating rate of 10^{o}C/min under 5% H_2 flow in argon (20 mL/min total flow).

2.4 Catalysis measurements

Isomerization of linoleic acid (>98% purity) was conducted in a stirred batch reactor (25mL) which was provided with a reflux condenser and a heating jacket. In a typical experiment, 10mL 1mol/L linoleic acid solvent and 0.4g catalyst were charged all at once. A nitrogen flow was fed through the reactor before and during the isomerization to have an inert atmosphere and the reactor outlet was locked by a fluid to prevent back-diffusion of oxygen into the reactor. The system was stirred at 400rpm in the experiments to keep the catalyst uniformly dispersed in the reaction medium, and also to eliminate external mass-transfer problems. Catalytic tests were performed at 180 ^{o}C for 2h. For reusability of the catalysts, spent catalyst was washed with n-hexane to remove adsorbed reactant/products from the surface of catalysts. After that the catalyst was dried for 10h at 80^{o}C and reused for isomerization reaction.

2.5 Products analysis

The sample from the reactor was methyl esterification by using BF_3-methanol [22]. After methyl esterification, 20uL of the sample was dissolved in 1mL isooctane, then it was analyzed by a gas chromatograph (GC, Agilent 7890A) equipped a 100m HP-88 column (inner diameter: 0.25mm and film thickness: 0.25μm), flame ionization detector (FID) unit, and an autosample injector. Injector and detector temperature were 240 ^{o}C. The column temperature was maintained at 120 ^{o}C for 1min, and then increased at 10 ^{o}C/min to 175 ^{o}C and held there for 15min and then increased at 5 ^{o}C /min to 210 ^{o}C and held there for 5min and then increased at 5 ^{o}C /min to 230 ^{o}C and held there for 5min. Heptadecane was used as the internal standard. Most *CLA* isomers were identified based on retention times, using standard references. Other *CLA* isomers were identified based on literature data [23].

3. Results and Discussion

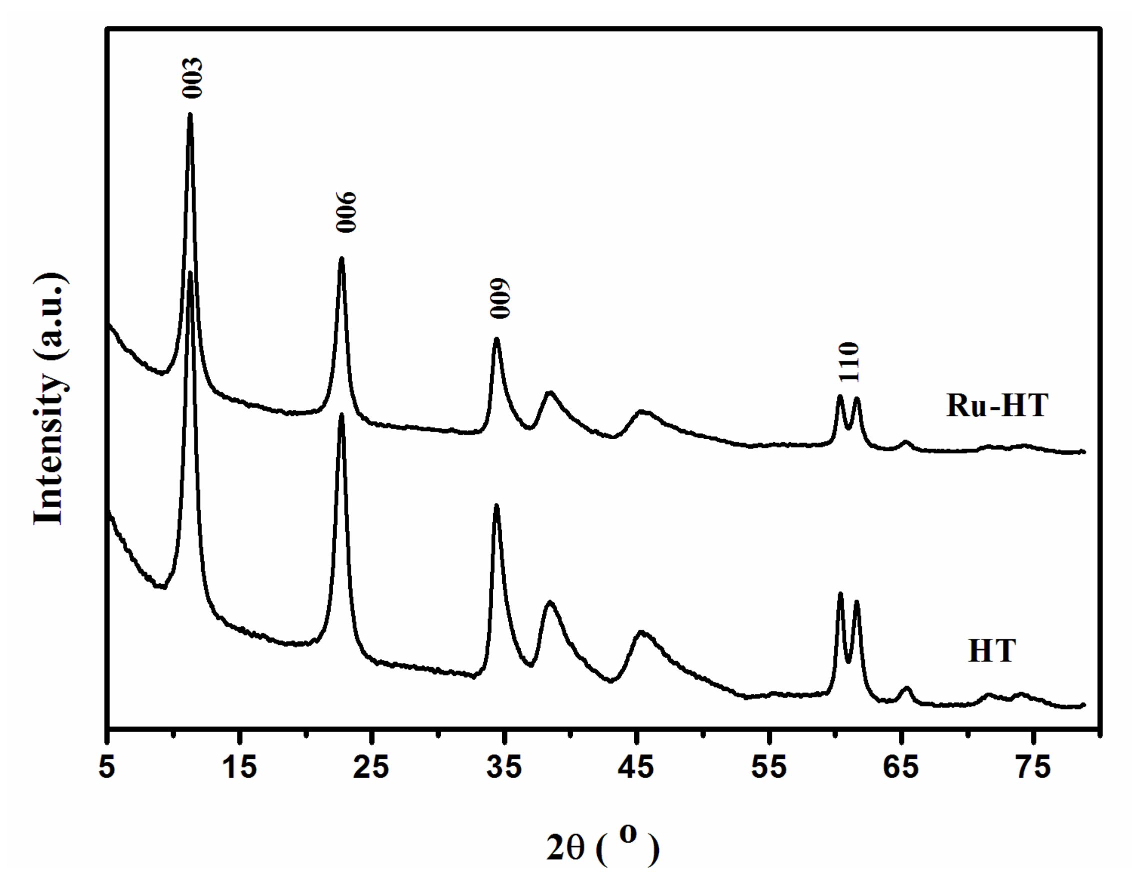

Fig.1 The XRD patterns of Ru-HT and HT

Table.1. Physical characterization of HT and Ru-HT samples.

Samples	Unit cell parameter(*a*), Å	Unit cell parameter(*c*), Å	Crystallinity,%
HT	3.062	23.50	100
Ru-HT	3.066	23.47	85

The XRD patterns of the as-synthesized HT and Ru-HT are shown in Fig.1. For the Ru-HT, the diffraction peaks are typical characteristics of the hydrotalcite (JCPDS file NO.14-0191), indicating that Ru-HT was successfully prepared. These reflections at respective 2θ are no difference and revealed a good dispersion of ruthenium. The intensities of (003) and (006) planes, which are directly related to the crystallinity were observed to decrease to 85% for Ru-HT samples as compared to pristine HT (Table 1). Decrease in the crystallinity on introducing the ruthenium cations in hydrotalcite structure could be attributed to the increase in the number of cations of higher ionic radii in brucite sheet. Increase in the value of *a* was also observed for Ru-HT sample (3.066 Å) as compared to HT sample (3.062 Å) due to larger ionic radii of ruthenium (0.68 Å) as compared to aluminum (0.53 Å). Decrease in the value of unit cell parameter *c* was observed for Ru-HT sample (23.47 Å) as compared to the value for HT (23.50 Å). This results into decrease in charge density on layers due to weaker interaction (or decrease in Coulombic attractive force) between the negatively charged interlayer anions and positively charged brucite like layers [20]. All above features indicate that ruthenium was incorporated in the hydrotalcite layers.

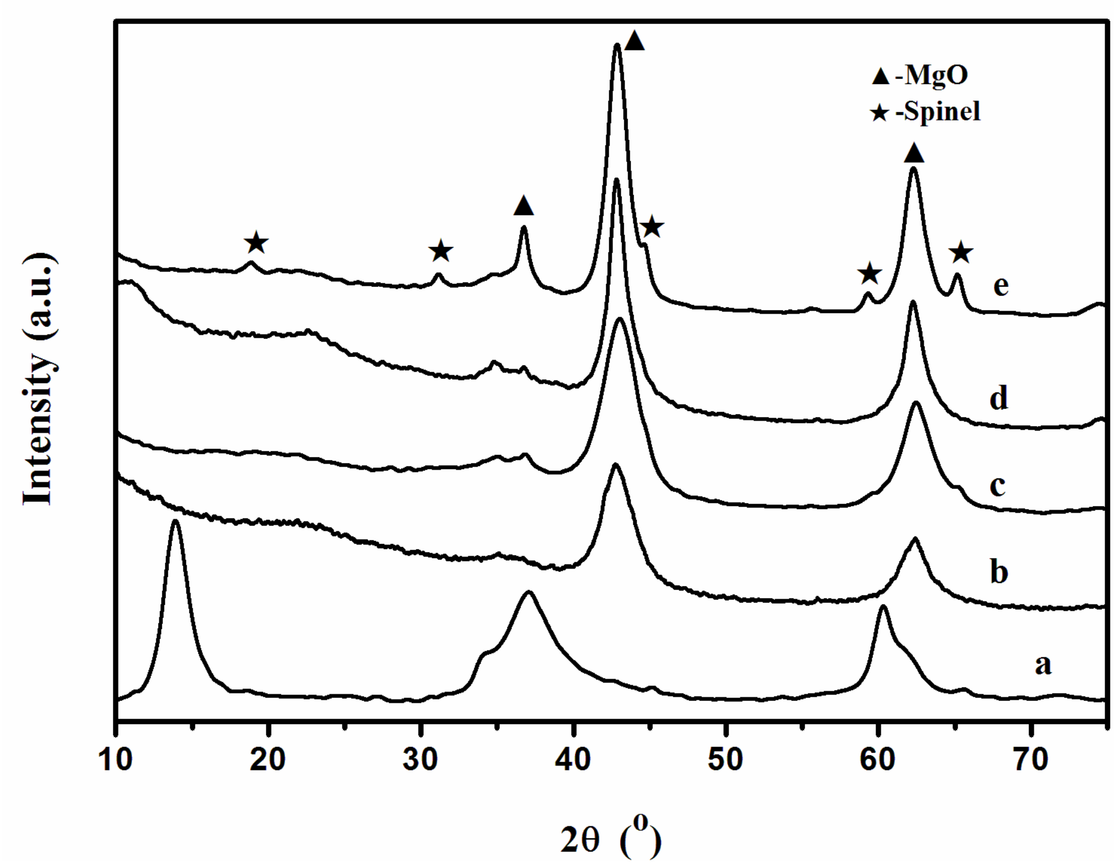

Fig.2 The XRD patterns of Ru-MgAl350(a), Ru-MgAl400(b), Ru-MgAl450(c), Ru-MgAl550 (d), Ru-MgAl700 (e)

The XRD patterns (Fig.2) of sample thermally at various temperature revealed that the layered structure of hydrotalcite destroyed in the temperature range of 350- 400 °C. For those calcined at 450 °C and higher temperature, the diffraction peaks corresponding to MgO and $MgAl_2O_4$ spinel can be observed, which indicated that the hydrotalcite completely transformed into composite oxides at the temperature above 450 °C. Moreover, when calcination temperature increased, the peak positions of MgO and spinel did not change, which indicated the good stability of composite oxide derived from the Ru-HT hydrotalcite [24].

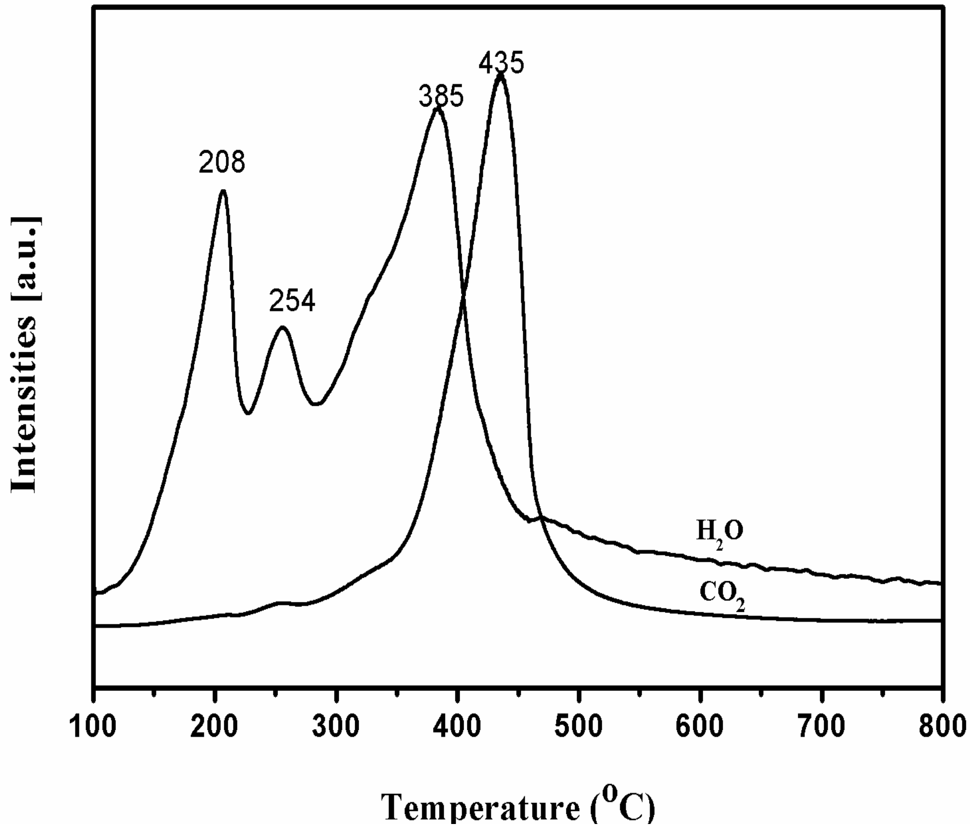

Fig.3. EGA-MS profiles of evolution of the gaseous products of the thermal decomposition of interlayer anions built in Ru-HT.

The evolution of the gaseous products formed during the thermal decomposition of the interlayer anions incorporated in the studied Ru-HT is shown in Fig.3. The two peaks 208 ^{o}C and 254 ^{o}C corresponded to the elimination of physically adsorbed water and interlayer water; the third peak of 385 ^{o}C can be ascribed to the removal of OH- from the brucite-like layer as water molecules [25]. Simultaneously, it is clear that CO_3^{2-} anions are transformed into CO_2, which leaves the material starting from about 250 ^{o}C, the maximum of CO_2 evolution rate is at about 435 ^{o}C.

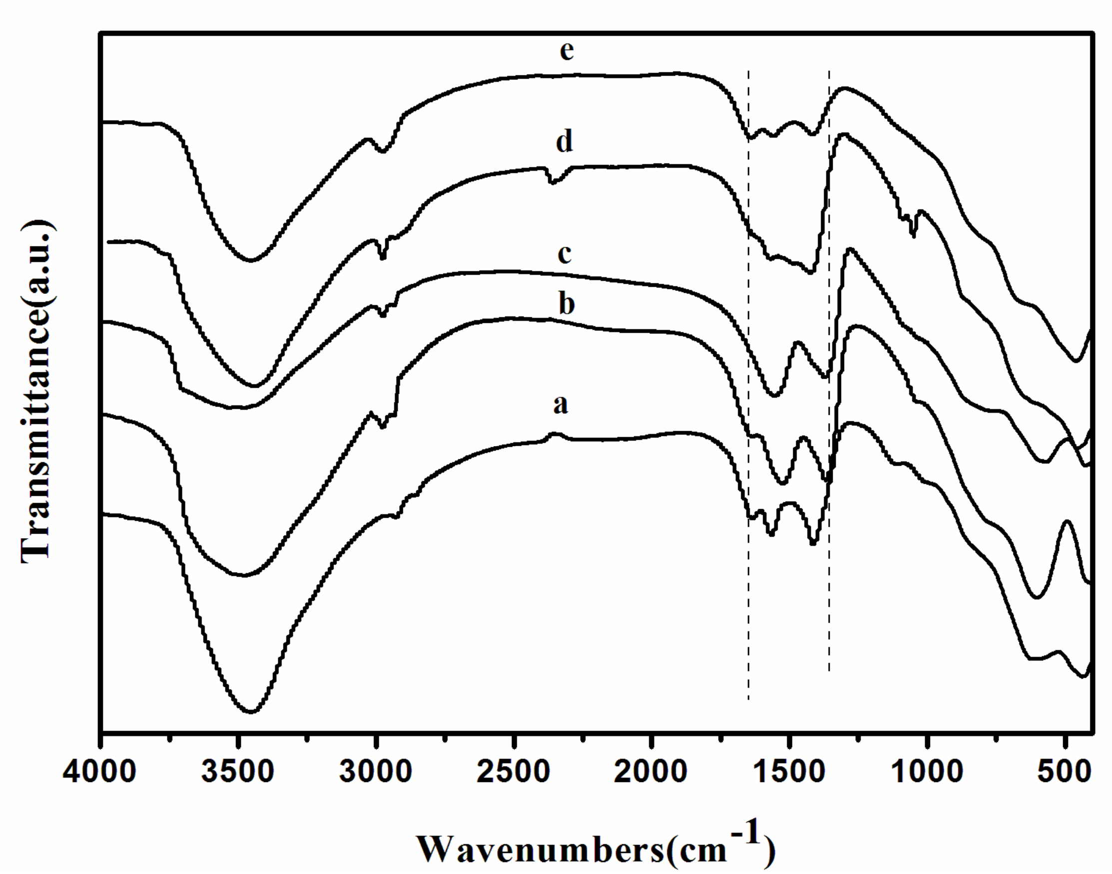

Fig.4 The FTIR spectra of Ru-HT(a), Ru-MgAl350(b), Ru-MgAl400(c), Ru-MgAl450(d), Ru-MgAl700(e)

In order to better understand the change on the functional group of Ru-HTs during calcination, FTIR (Fig.4) measurements have been carried out. The FTIR spectrum of the uncalcined sample is typical of HTLCs compounds containing mainly carbonate anions. Three general types of IR-active vibrations of hydrotalcites can be distinguished: molecular vibrations of the hydroxyl groups, lattice vibrations of the octahedral layers and vibrations of the interlayer species. The band observed at $1360 cm^{-1}$ is attributed to the v_3 asymmetric stretching of the carbonate anions. Compared with the FTIR spectrum of the uncalcined sample, remarkable changes are observed in the IR spectra of HTLCs calcined at 350 °C and 400 °C. Some authors [26] have observed this rearrangement of carbonate anions during thermal annealing, and, in general, it happens along with the anionic grafting. The grafting of the anions with the layer leads to the formation of a new layered phase with an interlayer distance smaller than that observed in the parent sample. This assumption is supported by XRD results and discussion. When the calcination temperature increased to 450 ^{o}C, remarkable changes are observed. The 1360cm^{-1} band disappear completely. It can be indicated that the carbonate anions was removed when being calcined above 450 ^{o}C. The bending mode H-O-H from H_2O was observed at 1640cm^{-1} thus confirming the presence of water in the interlayer space. No significant changes within these ranges were observed in the spectra of calcined HTLCs (Fig.4 b, c, and d). It showed that calcination did not reduce the number of hydroxyl groups. On the other hand, the bands in the region below 1000cm^{-1}, which can be assigned to the M-O (M=Zn, Ni and Al) vibrations, is fully agrees with the description in the literature [20]. The FTIR study entirely consistent with the results obtained by means of the TPP-MS and XRD.

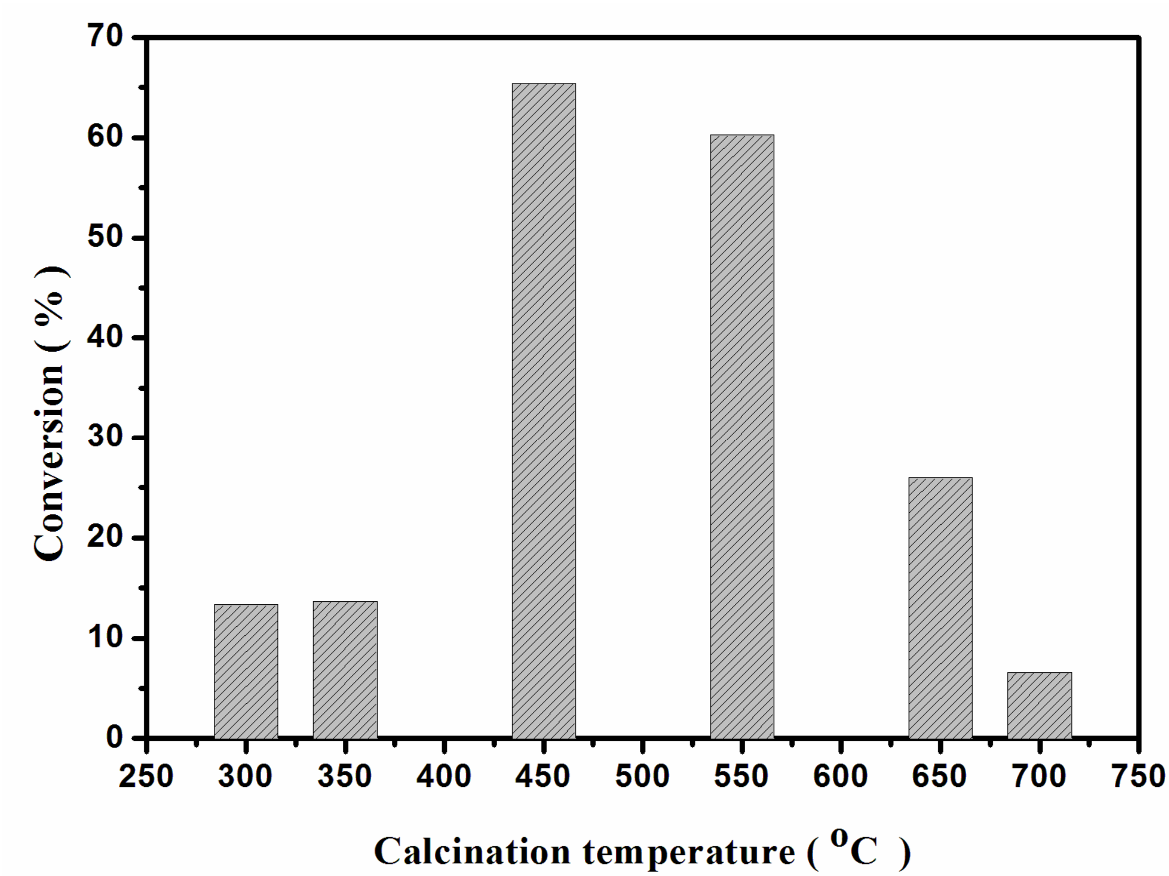

Fig.5. Effect of calcination temperature on CLA conversion. Reaction temperature 180^{o}C, catalyst weight 0.4g, reaction time 2h, 10mL1M LA solution.

The composite oxides were used to isomerize linoleic acid to conjugated linoleic acid. Fig.5 showed the *CLA* conversion as a function of catalysts calcination temperature, suggesting that the calcination temperature has a marked effect on the catalyst activity. In the range of 350 ^{o}C to 450 ^{o}C, the activity of the catalyst increased with the increasing calcination temperature. The catalyst calcined at 450 ^{o}C exhibited the best excellent catalytic activity. However, the catalyst activity sharply dropped when the temperature increased to 550 ^{o}C and higher. For Ru-MgAl450, the 65% conversion was observed while only 7% conversion was sustained for Ru-MgAl700.Generally speaking, high surface area of catalyst would provide more surface area for active sites and higher chances for the catalysts to be exposed to reactant molecule. However, it's worth mentioning that Ru-MgAl350 and Ru-MgAl400' activities were much lower than Ru-MgAl450 though their surface area (Table 2)were higher than it, which indicated that the surface area was not the main factor responsible for the catalytic activity. Base on the above XRD and FT-IR characterization, we think that at low calcination temperature, the transition to Ru-MgAls from Ru-HT has not fully formed; the linoleic acid molecules could not be fully close to the active sites due to the limitation of interlayer groups. As the calcination temperature increased, the carbonate anions were completely removed, which resulted in the exposed active sites on the surface of the catalysts. Besides, the crystal gradually tended to reach perfection, thus the catalytic activity was increased. However, when the calcination temperature was increased higher, the catalytic activities were decreased, especially for the Ru-MgAl700 sample, the LA conversion was only 7%. Obviously, others factor may affect their catalytic activity.

Table.2. Specific Surface Area of Catalysts at Different Calcination Temperature

Sample	Ru-HT	Ru-MgAl350	Ru-MgAl400	Ru-MgAl450	Ru-MgAl550	Ru-MgAl700
Specific surface area(m^2/g)	79	112	177	155	138	116

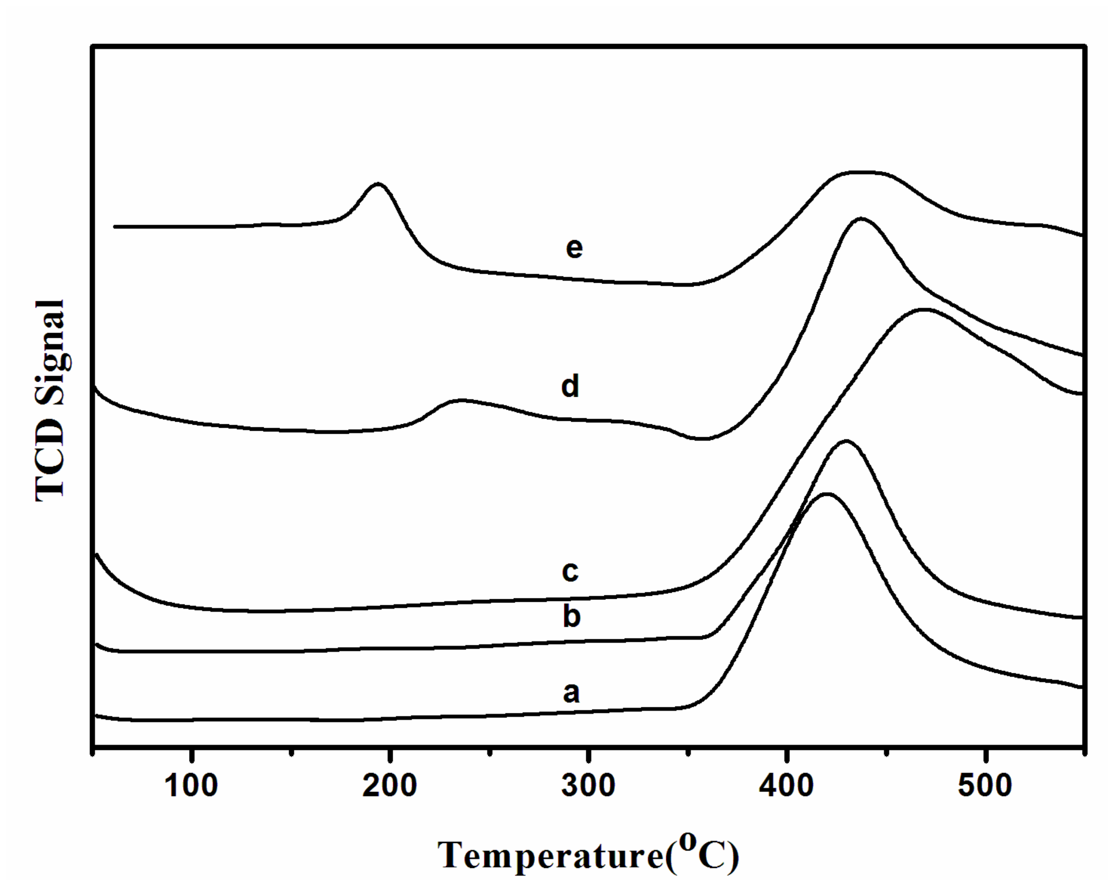

Fig.6. The H_2-TPR profiles of Ru-MgAl350 (a), Ru-MgAl400 (b), Ru-MgAl450(c), Ru-MgAl550 (d), Ru-MgAl700 (e).

Fig.6. shows H_2-TPR profiles of the Ru-HT samples calcined at different temperature. For Ru-MgAl350, Ru-MgAl400 and Ru-MgAl450, there is only a broad reduction peak with maximum at around 450°C, respectively. The peak can be assigned to the reduction of RuO_2 [27-28]. Thus it could be stated that when the Ru-HT samples is calcined below 450 °C, a few amount of ruthenium is segregated as RuO_2, most of the oxidized ruthenium species are well-stabilized in the catalyst matrix. Moreover, this reduction temperature is much higher than that found for bulk RuO_2, and apparently indicates that a strong interaction of the ruthenium species exists with the support. Obviously, one could be found that in the series of samples calcined from 350 to 450 °C, the stronger interaction of ruthenium species with the support, the better the catalytic

performances was. As increasing the calcination temperature from 550 °C to 700 °C, a new reduction peak appears in the low temperature, which may be attributed to the reduction of bulk RuO_2, thus suggesting a larger metallic particle size. This behavior may be explained ruthenium atoms segregate to minor quantities of RuO_2 [29]. Clearly, that ruthenium atoms segregate to RuO_2 is unfavourable for the catalysis activity; the catalysis activity of Ru-MgAl700 is much lower than that of Ru-MgAl450 and even lower than that of Ru-MgAl350. Thus the ruthenium has a profound effect on the catalytic performance of the series of Ru-MgAl catalysts.

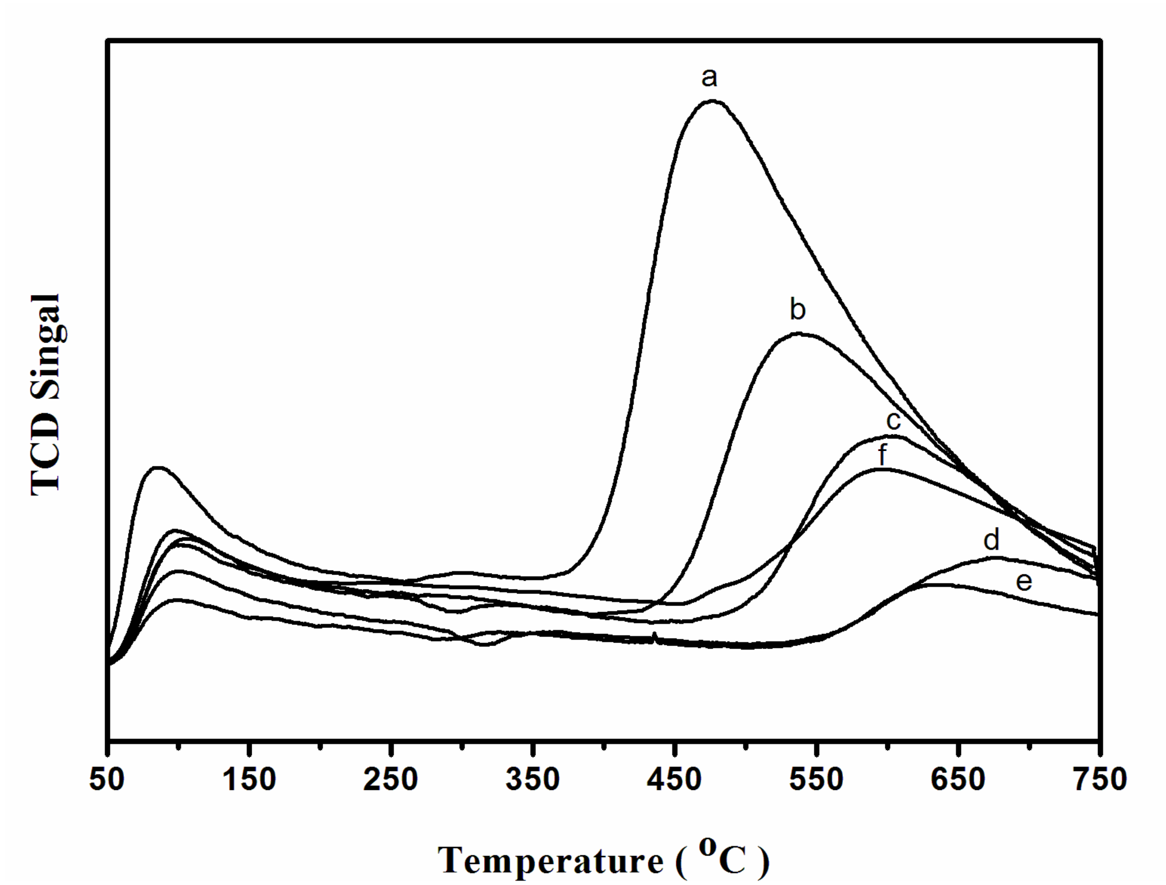

Fig.7. The CO_2-TPD profiles of Ru-MgAl350 (a), Ru-MgAl400 (b), Ru-MgAl450(c), Ru-MgAl550 (d), Ru-MgAl700 (e), MgAl-450 (f).

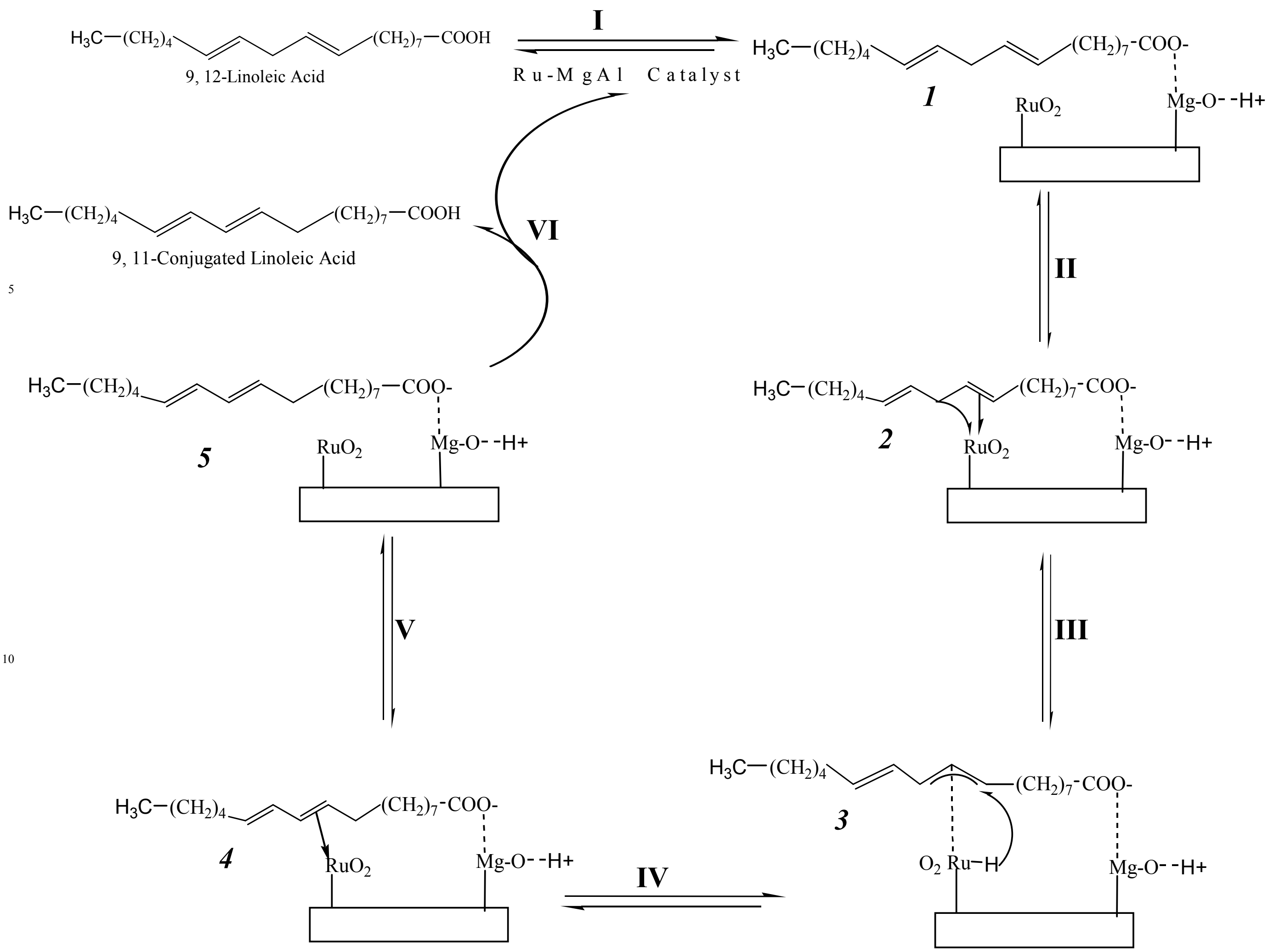

Fig.8. Possible reaction mechanism for the isomerization of linoleic acid to conjugated linoleic acid using Ru-MgAl catalyst

It was reported that the basicity of catalysts played a decisive role in the double bond isomerization, which has been suggested to proceed via a carbanion intermediate on the basic sites and then transferred to the terminal production[30].The basicity of the series of Ru-MgAl oxides has been determined using CO_2-TPD technique (Fig.7). This technique affords information about the strength and amount of basic sites from desorption temperature and the peak area, respectively. In all cases, the graphs exhibit two desorption peaks, between 50 and 150 ^{o}C and from 370 until 680 ^{o}C. The differences of the first desorption temperature for all the samples were small, but the second desorption peak shift toward high temperature as the calcination temperature increased from 350 ^{o}C to 550 ^{o}C, which indicated that the strength of basicity of Ru-MgAl increased with the rise of calcination temperature, and the Ru-MgAl550 sample exhibits the highest basicity among this family of catalysts. Interestingly, the same trend has taken place in the above linoleic acid isomerization reaction (Fig.5), namely, the catalysis activity increased with the strength of basicity of catalysts; it seems that the catalytic activity is related to the basicity strength of the catalyst. However, some interesting results were found. When we used Ru-Al450 which was reported to have a few basicity amounts as catalyst (Table 3, entries10), the CLA yield was very low. In addition, when methyl linoleate was used as the reactant (Table 3, entries11), the CLA yield was almost approaching zero. The above two tests revealed that the basic sites of the catalysts were very important for the isomerization, but it is not the only decisive role. We therefore suppose that the basic site maybe plays an absorption role. To identify the active centers responsible for the isomerization reaction, another test was performed by using MgAl450 devoid of ruthenium, the *CLA* yield was also approaching zero, (Table 3, entries12). It is worth mentioning that the basic strength and the basic amount (Fig.7c and f) for the Ru-MgAl450 and MgAl450 were almost equal. Hence, those above facts let us to think that the basicity sites of catalyst and ruthenium could have a synergic effect on the catalytic activity, namely, the Ru-MgAl was a bifunctional catalyst where the catalyst not only provided the basic sites, but also provided the noble metal activity sites necessary in the isomerization reaction. What's more, the basic site plays an absorption role and the ruthenium activity site responsible for the double bond migration reaction. According to the above facts, the possible reaction mechanism for the isomerization of linoleic acid to conjugated linoleic acid was proposed as follows (Fig.8): initially, the linoleic acid was absorbed on basic sites of the solid base surface (step I). The next step II is the interaction electron of ***1*** to form a π-complex ***2*** with RuO_2. The equilibrium step III gives π–allyl metal complex ***3*** through allyl-H-migration from γ-carbon atom to metal. The hydride shift from π-allyl metal-hydride complex ***3*** to

α-carbon atom gives complex ***4*** via next equilibrium step IV. The dissociation of active catalyst species from the complex ***5*** results the formation of conjugated linoleic acid.

Table.3. Comparison of different catalysts described in the literature for the production of CLA in different reaction atmosphere (RAs).

Entry	Substrate	Catalyst	Solvent	T[^{o}C]	RA	Y_{CLA}[a]%	P[b]	R[c]	TOF[d]	Ref.
1	methyl linoleate	KOH	ethylene glycol	180	N_2	97	0.63	-	-	[18]
2	methyl linoleate	Ru/C	n-decane	250	N_2	31	0.019	13.6	5.3	[18]
3	linoleic acid	Ru/C	n-decane	165	N_2	58	0.90	23	17.2	[18]
4	linoleic acid	Ru/Al_2O_3	n-decane	165	N_2	30	0.0048	0.83	0.85	[18]
5	linoleic acid	Ru/H-Y	n-decane	120	N_2	24	0.002	0.8	0.4	[18]
6	linoleic acid	Ag/SiO_2	n-decane	165	H_2	67	0.021	1.5	0.7	[18]
7	linoleic acid	Au/C	n-decane	150	H_2	4	0.0005	0.2	0.1	[18]
8	methyl linoleate	Ru/Cs-USY	n-decane	165	N_2	75	0.391	234	99.8	[18]
9	linoleic acid	Ru-MgAl450	n-decane	180	N_2	65	1.4	438	102.6	this work
10	linoleic acid	Ru-Al450	n-decane	180	N_2	5	0.108	33.7	7.9	this work
11	methyl linoleate	Ru-MgAl450	n-decane	180	N_2	≈0	-	-	-	this work
12	linoleic acid	MgAl450	n-decane	180	N_2	≈0	-	-	-	this work

[a] Yield of CLA. [b] CLA productivity [g (CLA) L^{-1} (solvent) min^{-1}]. [c] CLA production rate [g (CLA) g^{-1} (Ru) h^{-1}]. [d] Turnover frequency [mol (LA converted) mol^{-1} (Ru) h^{-1}]. [e] The Ru-content of the catalyst was detected by XRF=0.8%.

Comparison of the production of *CLA* for different catalysts in different reaction atmospheres described in the literature was showed in Table 3. Most of the catalysts except Ru/Cs-USY showed low productivity. However, the productivity and TOF of Ru-MgAl450 reached 1.52g (*CLA*) L^{-1}(solvent) min^{-1} and 102.6mol (LA converted) mol^{-1}(Ru) h^{-1}). What's more, the productivity of Ru-MgAl450 could even be comparable to that of the homogeneous process used industrially today. It is important for a heterogeneous catalyst with high selectivity to form physiologically *CLA* isomers. Fig.9

shows the *CLA* isomers determined by GC analysis. Peak identifications for three CLAs were confirmed by spiking with standard *CLAs*. The result indicates that three major *CLA* isomers were formed during the conjugation reaction, namely, *c9, t11-CLA (14%)*, *t10, c12-CLA* (16%) and *t9, t11-CLA* (35%). Their retention time are 25.680, 25.994, 26.681min, respectively. Other *CLA* isomers were also formed, but the amounts were small. The above results indicate that the catalyst shows high selectivity for desirable *c9, t11-*, *t10, c12-* and *t9, t11-CLA* isomers.

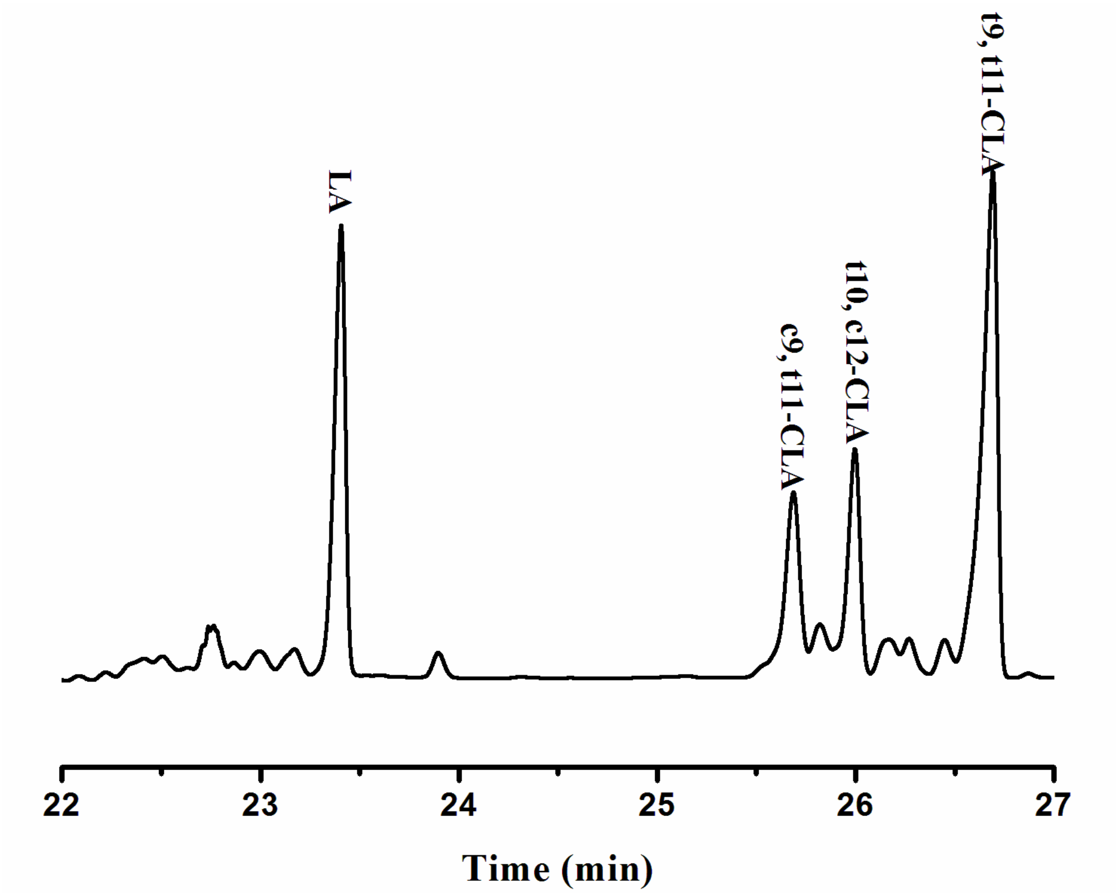

Fig.9. Gas chromatogram of the isomerization produces from linoleic acid.

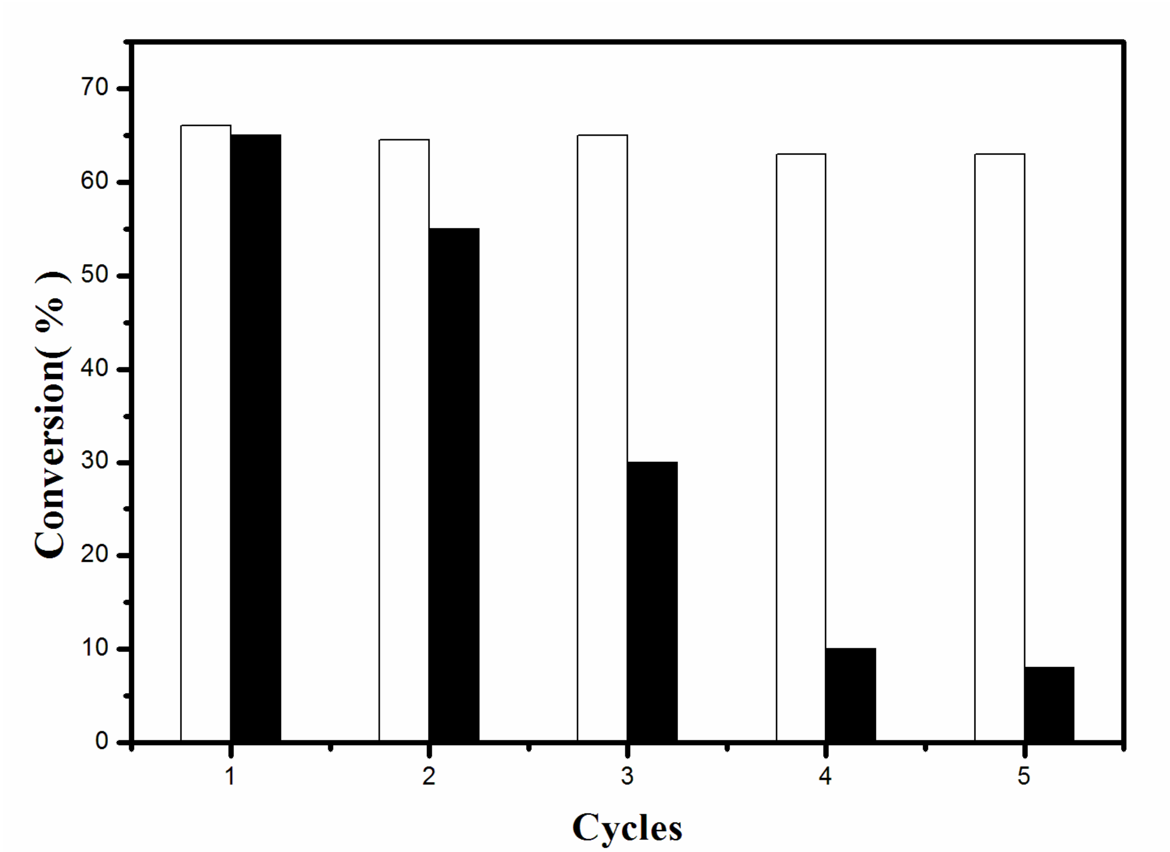

Fig.10. Reusability of catalysts for isomerization of linoleic acid (gray= Ru-MgAl450, black= impregnated Ru-catalyst)

For a catalyst, the reusability in a sense is more important than activity. The optimal Ru-MgAl450 catalyst was tested in a recycling experiment. Conversion for isomerization of linoleic acid was observed to remain unchanged even after the fifth run (Fig.10), confirming that the catalyst was reusable for the isomerization reaction without loss in its activity. In the first run, the catalytic activity of sample synthesized by impregnation of ruthenium on hydrotalcite was similar to that of Ru-MgAl450 sample. However, the conversion rate of linoleic acid decreases sharply after the second run which might be due to the leaching of ruthenium from support. This suggests that the substitution of ruthenium for Mg or Al cations increases the stability of catalysis, which makes Ru-MgAl an active and reusable catalyst.

4. Conclusions

The Ru-MgAl composite oxides catalysts prepared by thermal decomposition of ruthenium grafted hydrotalcite were used to isomerization of linoleic acid to conjugated linoleic acids without hydrogen. Results indicated that the catalyst calcined at 450 ^{o}C showed the highest catalytic activity, compared with other heterogeneous processes reported in the literature, higher productivities of and selectivities for *CLA* can be obtained. The Ru-MgAl was a bifunctional catalyst and the basicity sites and ruthenium had a synergic effect on the catalytic activity; meanwhile, the basic site plays an absorption role in the isomerization reaction, and the ruthenium activity site responsible for the double bond migration reaction. Because it had high productivity as well as durability and it also produced beneficial *CLA* isomers products, the catalyst of Ru-MgAl450 is suitable for the isomerization of linoleic acid to conjugated linoleic acid; this research may also accelerate the development of *CLA*-enriched functional foods.

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