Ruthenium containing hydrotalcite as a solid base catalyst for >C=C< double bond isomerization in perfumery chemicals

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ABSTRACT

Ruthenium containing hydrotalcite (Ru–Mg–Al) is used as a solid base catalyst for >C=C< double bond isomerization of methyl chavicol, eugenol, safrole, allylbenzene, dimethoxy allylbenzene and 3-carene. The catalyst showed excellent conversion and selectivity for isomerization reaction in shorter reaction time (2 h). Catalytic activity and reusability of Ru–Mg–Al was compared with ruthenium impregnated catalysts such as, Ru–HT, Ru–MgO, Ru–CaO, Ru–SiO$_2$ and Ru–alumina for isomerization of methyl chavicol to *trans*-anethole. Ru–Mg–Al catalyst was reused four times without loss in its activity, however, significant loss in the conversion of methyl chavicol and selectivity of *trans*-anethole was observed on reusability of other ruthenium impregnated catalysts. The conversion of methyl chavicol and selectivity of *trans*-anethole was found to increase on increasing the reaction temperature as well as amount of catalyst. At 0.005 g catalyst amount, 55% conversion of methyl chavicol with 68% selectivity of *trans*-anethole was observed that increased to 93% with 82% selectivity of *trans*-anethole at 0.05 g catalyst amount. On further increase in the amount of catalyst to 1 g, conversion increased to 98% with 88% selectivity of *trans*-anethole.

1. Introduction

>C=C< double bond isomerization reaction is of great interest because of its potential commercial applications for the synthesis of fine and perfumery chemicals [1]. For example, *trans*-anethole is a valuable perfumery chemical [2,3] and intermediate for the synthesis of other chemicals. Synthetically, *trans*-anethole is produced via double bond isomerization of methyl chavicol [4] using strong liquid base like potassium hydroxide and sodium hydroxide used in stoichiometric amounts. Highest conversion of methyl chavicol (56%) with 82:18 *trans*- to *cis*-anethole ratio has been reported in 12 h at 200 °C [4]. However, this method suffers from drawbacks like, post-synthesis work-up to separate spent KOH or NaOH from reactant/product mixture, use of solvent, longer reaction time and lower conversion. Therefore, it is desirable to develop an environmentally benign catalytic process for the solvent free synthesis of *trans*-anethole via double bond isomerization of methyl chavicol in a shorter reaction time.

In our earlier reports, transition metal complexes of rhodium, ruthenium and palladium were demonstrated as potential catalysts for double bond isomerization of methyl chavicol to *trans*-anethole

and eugenol to *trans*-isoeugenol in homogeneous reaction conditions [5,6]. In another study, hydrotalcite, ion exchanged zeolites were used as catalysts for isomerization of methyl chavicol in 10 h reaction time [7]. Kishore and Kannan studied the catalytic activity of as-synthesized hydrotalcite having divalent and trivalent metals in varied ratios for isomerization of eugenol [8], safrole [9,10] and estragole [11] in various polar and non-polar organic solvents. In another study, hydrotalcite of different compositions and varied divalent to trivalent cations ratio were used as catalysts for the isomerization of methyl chavicol and eugenol in the presence of dimethyl formamide (DMF) as a solvent [8,11]. Conversion of eugenol was achieved up to 75% with 85% selectivity of *trans*-isoeugenol in 6 h at substrate to catalyst ratio 2:1. The main drawbacks of these studies are the use of DMF as a solvent, very low substrate to catalyst ratio, non-reusability of catalyst and lower conversion using impregnated catalyst.

Hydrotalcite or layered double hydroxides (HT; $[M(II)_{1-x}M(III)_x(OH_2)]^{x+}(CO_3{}^{2-})_{x/n} \cdot mH_2O$; where M(II) = Mg or divalent cation and M(III) = Al or trivalent cation) is an attractive catalyst due to the availability of wide variety of basicity which can be achieved by proper tuning of the M(II) and M(III) molar ratio, intercalation of suitable anion in the interlayer space or activation of hydrotalcite at 450 °C. Various metals can be introduced into the brucite layer via isomorphic substitution of M(II) or M(III) cations at the octahedral sites, which are expected to be the active sites for organic transformations [12,13]. Ruthenium incorporated

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hydrotalcite samples are reported to be highly active catalyst for oxidation of alcohols and aromatic compounds [14], direct alkylation of nitriles with primary alcohols [15] and for the one-pot synthesis of quinolines [16]. Apart from these applications, the literature is silent on the potential of ruthenium containing hydrotalcite as a catalyst for various organic transformations.

The present manuscript describes the use of ruthenium containing hydrotalcite (Ru–Mg–Al) as a reusable eco-friendly catalyst for solvent free double bond isomerization in perfumery chemicals such as methyl chavicol, eugenol, safrole, allylbenzene, dimethoxy allylbenzene and 3-carene (Scheme 1).

2. Experimental

2.1. Materials

Magnesium chloride [$MgCl_2 \cdot 6H_2O$; 98%], aluminum chloride [$AlCl_3 \cdot 9H_2O$; 98%], sodium carbonate [Na_2CO_3; 99.9%], sodium hydroxide [NaOH; 99.9%], silica [SiO_2; surface area = 200 m^2/g], CaO [surface area = 92 m^2/g], MgO [surface area = 130 m^2/g] and alumina [Al_2O_3; surface area = 192 m^2/g] were purchased from S.D. Fine Chemicals Ltd., Mumbai, India and used as received. Ruthenium trichloride [$RuCl_3 \cdot xH_2O$], methyl chavicol, eugenol, safrole, allylbenzene, 3-carene, dimethoxy allylbenzene and tetradecane (98%) were procured from Sigma–Aldrich, USA and used without further purification. The double distilled milli-pore deionized water was used for the synthesis of catalysts.

2.2. Catalyst preparation

2.2.1. Synthesis of ruthenium hydrotalcite [Ru–Mg–Al]

Ruthenium grafted hydrotalcite was prepared by co-precipitation method at a constant pH [12]. In a typical synthesis procedure, an aqueous solution (A) containing $MgCl_2 \cdot 6H_2O$ (0.0522 mol), $AlCl_3 \cdot H_2O$ (0.0144 mol) and $RuCl_3 \cdot xH_2O$ (0.5 mmol) in 50 mL double distilled deionized water was prepared. The solution A was added drop wise into a second solution (B) containing Na_2CO_3 (0.079 mol) in 50 mL double distilled deionized water, in around 45 min under vigorous stirring at 30 °C. Constant pH of the mixture was maintained by adding 1 M NaOH solution. Content was then transferred into the teflon coated stainless steel autoclave and aged at 80 °C for 16 h under autogenous water vapor pressure. After 16 h, the precipitate formed was filtered and washed thoroughly with hot distilled water until the filtrate was free from Cl^- ions as tested by silver nitrate solution. The obtained filter cake was dried in an oven at 80 °C for 14 h. The solid material (yield = 5.1 g) named as Ru–Mg–Al, was ground and stored under vacuum. The activation of Ru–Mg–Al was carried out in a muffle furnace at 450 °C for 4 h. Synthesis of Mg–Al hydrotalcite sample with Mg/Al molar ratio of 3.5 [HT(3.5)] was done as per the above-mentioned procedure without use of $RuCl_3 \cdot xH_2O$ solution.
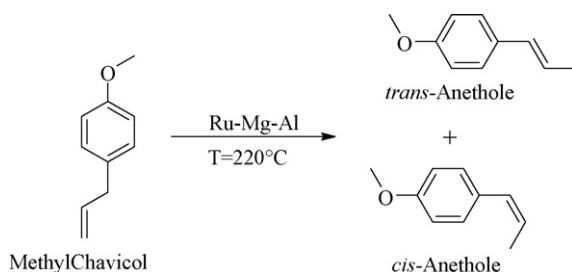
2.2.2. Synthesis of ruthenium impregnated catalysts

Impregnation of ruthenium (Ru) metal on solid base supports namely HT(3.5), MgO, CaO, alumina, SiO_2 was carried out to compare the catalytic activity of Ru-impregnated catalysts with Ru–Mg–Al by the following procedure. An aqueous solution of $RuCl_3 \cdot xH_2O$ (0.5 mmol) in 40 mL deionized double distilled water was added drop wise to the suspension of 5.1 g of respective solid support in 40 mL water under N_2 atmosphere. The mixture was vigorously stirred for 16 h at 30 °C. The slurry was filtered and washed with hot distilled water until the filtrate was free from Cl^- ions (silver nitrate test). Then the filter cake was dried at 80 °C for 14 h.

2.3. Characterization of catalysts

Powder X-ray diffraction (P-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 5–70°. Operating voltage and current were kept at 40 kV and 40 mA, respectively. The percentage crystallinity of HT(3.5) and Ru–Mg–Al were calculated by the summation of integral intensities of diffraction peaks corresponding to (0 0 3) and (0 0 6) planes. The values of unit cell parameters (a and c) of HT(3.5) and Ru–Mg–Al samples were calculated by the formula: $a = 2(d_{110})$ and $c = 3(d_{003})$; where d_{110} and d_{003} are the basal spacing values of (1 1 0) and (0 0 3) planes respectively [17].

Fourier transform infra-red (FT-IR) spectra of synthesized catalysts were recorded with a PerkinElmer Spectrum GX FT-IR spectrometer in the region of 400–4000 cm^{-1} using KBr pellets. Thermogravimetric analysis (TGA) of HT(3.5) and Ru–Mg–Al samples were carried out using a Mettler Toledo TGA/SDTA 851e equipment in nitrogen flow (flow rate = 50 mL/min) at a heating rate of 10 °C/min and the data were processed using star^e software. Surface area of synthesized catalysts was measured using ASAP 2010 Micromeritics, USA. The samples were activated at 120 °C for 4 h under vacuum (5×10^{-2} mmHg) prior to N_2 adsorption measurements. The specific surface area of the samples was calculated from N_2 adsorption isotherms measured at 77.4 K as per Brunauer, Emmett, Teller (BET) method. Chemical analyses of the catalysts were carried out using Inductive Coupled Plasma (ICP) Spectrometer, PerkinElmer, Optima 2000 instrument.

2.4. Isomerization reaction and products analysis

For the double bond isomerization reactions, calculated amount of reactant and catalyst were taken with 0.01 g tetradecane (used as an internal GC standard) in a 25 mL double necked round bottom flask. One neck of the flask was fitted with refluxing condenser and another neck of the flask was blocked with silicon rubber septa. The flask was kept in an oil bath equipped with temperature and agitation speed controllers and the reaction was carried out under nitrogen atmosphere. The analysis of product mixture was carried out by gas chromatography (GC; Shimadzu 17A, Japan), having 5% diphenyl and 95% dimethyl siloxane universal capillary column (60 m length and 0.25 mm diameter) and flame ionization detector (FID). The initial column temperature was increased from 100 to 220 °C at the rate of 10 °C/min using nitrogen as a carrier gas. The temperature of injection port and FID were kept at 250 and 300 °C, respectively, during the analysis of product mixture. The retention times for each compound were determined by injecting pure compound under identical GC conditions.

Experiments were repeated under identical reaction conditions to ensure the reproducibility of the reaction. Conversion and selectivity data were found to be reproducible within ±2% variation. For kinetic studies, samples (0.1 mL) were taken out during the course of experiment using glass syringe at different time intervals. For reusability of the catalysts, spent catalyst was washed with
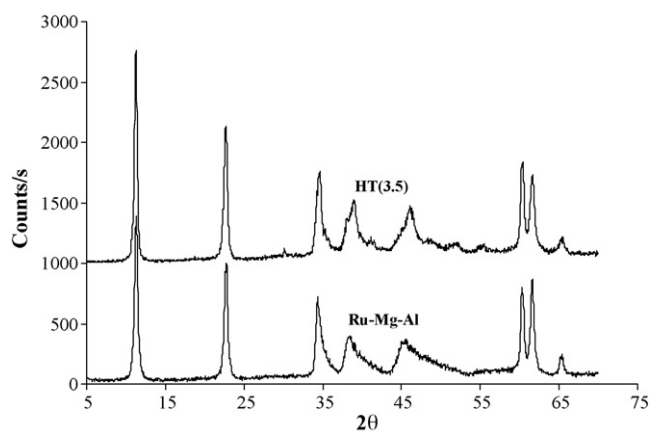

Scheme 1. Double bond isomerization of methyl chavicol.

Fig. 1. P-XRD patterns of HT(3.5) and Ru–Mg–Al samples.

Fig. 2. FT-IR spectra of HT(3.5) and Ru–Mg–Al samples.

methanol to remove adsorbed reactant/products from the surface of catalysts. After that the catalyst was dried for 10 h at 100 °C and reused for isomerization reaction.

3. Results and discussion

3.1. Characterization of catalyst

The sharp and symmetric reflections of (0 0 3) and (0 0 6) planes at low values of 2θ angles (11–23°) and broad, asymmetric reflections at higher 2θ angles (34–66°) were observed in the P-XRD patterns of HT(3.5) and Ru–Mg–Al samples (Fig. 1). These reflections at respective 2θ angles are typical characteristics of the hydrotalcite and revealed a good dispersion of aluminum and ruthenium in the brucite layers [18]. The P-XRD pattern of Ru–Mg–Al sample shows that the characteristic original planes of HT(3.5) are retained after incorporation of ruthenium in the brucite sheet. Presence of CO_3^{2-} anions in the interlayer space of HT(3.5) and Ru–Mg–Al samples was confirmed by the characteristic basal spacing of (0 0 3) plane; $d_{003} = 7.65$ Å. Any additional peaks corresponding to other crystalline phases were not observed in the P-XRD pattern of Ru–Mg–Al. The intensities of (0 0 3) and (0 0 6) planes, which are directly related to the crystallinity were observed to decrease to 88% for Ru–Mg–Al sample as compared to pristine HT(3.5) (Table 1). Decrease in the crystallinity on introducing the ruthenium cations in hydrotalcite structure (Ru–Mg–Al) 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–Mg–Al sample (3.069 Å) as compared to pristine hydrotalcite (3.064 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–Mg–Al sample (23.38 Å) as compared to the value for HT(3.5) (23.41 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 [12,16,18]. P-XRD patterns of Ru–HT(3.5), Ru–MgO, Ru–CaO,

Ru–alumina and Ru–SiO$_2$ were observed similar to their pristine counterparts (Fig. 1; Supporting Information).

FT-IR spectra of HT(3.5) and Ru–Mg–Al samples (Fig. 2) showed all the characteristic peaks of hydrotalcite structure [18,19]. The peak at around 3450–3480 cm^{-1} is due to the ν_{OH} mode of H-bonded hydroxyl groups in the layers and broadening of this peak is dependent on the strength of hydroxyl bonds. Shoulder present at 3000 cm^{-1} is attributed to the hydrogen bonding of hydroxyl groups of layered lattice and/or water molecules with interlayer carbonate anions [18]. Band that appeared at around 1640 cm^{-1} is due to the deformation mode of interlayer water molecules. Intensity of this band suggests the content of water molecules in the material. The sharp, intense vibrational band at around 1370 cm^{-1} is assigned to the asymmetric ν_3 mode of interlayer carbonate anions and absence of the band at around 1050 cm^{-1} suggests the retention of D$_{3h}$ symmetry of carbonate anions in the interlayer space. The bands in low frequency region (below 1000 cm^{-1}) are related with Mg–OH, Al–OH and Ru–OH vibrational modes in brucite-type layers. The bands at 950 cm^{-1} for the deformation of Al–OH and at 780 cm^{-1} for Al–OH translation were also observed. The peak at around 660 cm^{-1} (ν_4) is attributed to the in-plane carbonate bending. The band at 560 cm^{-1} is assigned to the translation modes of hydroxyl groups, influenced by Al^{3+} cations (Mg/Al–OH translation) [20]. The presence of band at 418 cm^{-1} is attributed to the Mg–OH vibrational mode.

Thermogravimetric analysis (TGA) curves of HT(3.5) and Ru–Mg–Al shown in Fig. 3 reveal two stage weight loss accompa-

Table 1
Physical characterization of the catalysts.

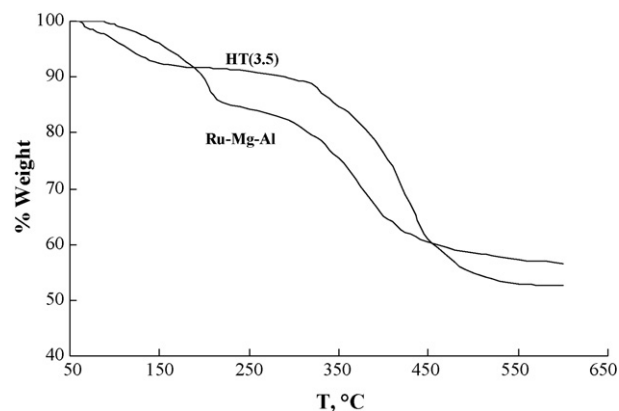|	HT(3.5)	Ru–Mg–Al
Crystallinity, %	100	88
Unit cell parameter (a), Å	3.064	3.069
Unit cell parameter (c), Å	23.41	23.38
W_1, %; (T_1, °C)	8; (80–160)	13; (180–220)
W_2, %; (T_2, °C)	36; (300–550)	26; (320–450)
Surface area, m^2/g	76	80

Fig. 3. TGA of HT(3.5) and Ru–Mg–Al samples.

nied by endothermal transformations. TGA curves of HT(3.5) and Ru–Mg–Al samples showed similar weight loss patterns. The 13% weight loss was observed in the Ru–Mg–Al sample at first stage (180–200 °C) which is attributed to the loss of physically adsorbed water molecules with relatively smaller amounts of condensed water molecules and CO_2. The 26% weight loss in second stage (300–450 °C) was observed due to removal of condensed water molecules and carbon dioxide from the carbonate anion present in the interlayer space of Ru–Mg–Al. During this temperature range, interlayer carbonate anions were thermally oxidized by a nearby interlayer water molecule to produce volatile CO_2 and interlayer hydroxyl anions. Observed lower weight loss in the Ru–Mg–Al sample as compared to HT(3.5) is due to the presence of ruthenium cations in the matrix of brucite sheet which led to higher thermal stability of the catalyst. Ruthenium content in the Ru–Mg–Al hydrotalcite sample was calculated by ICP and EDX analysis. The percentage ruthenium content in the Ru–Mg–Al hydrotalcite sample was found to be 1.0% (by wt).

BET surface area of HT(3.5) and Ru–Mg–Al samples was found to be 76 and 80 m^2/g, respectively (Table 1). Increase in the surface area for ruthenium containing hydrotalcite sample is attributed to the observed decrease in the crystallinity as compared to [HT(3.5)] sample which is also seen from P-XRD patterns. Surface area of other ruthenium impregnated samples, Ru–HT, Ru–alumina, Ru–MgO, Ru–SiO$_2$, Ru–CaO was found to be 82, 161, 92, 172, 80 m^2/g, respectively. The catalytic activity of Ru–Mg–Al was investigated for double bond isomerization of methyl chavicol to anethole, a base catalyzed reaction, by varying the amount of catalyst and reaction temperature.

3.2. Catalytic activity of Ru–Mg–Al for double bond isomerization of methyl chavicol

Catalytic activity of Ru–Mg–Al was evaluated for the isomerization of methyl chavicol to *trans*-anethole and the corresponding data on methyl chavicol conversion and *trans*-anethole selectivity are shown in Fig. 4. Conversion of methyl chavicol and selectivity of *trans*-anethole was observed to increase with increase in the amount of catalyst up to 0.1 g. On further increase in the amount of catalyst, no significant effect on conversion and selectivity of *trans*-anethole was observed. Therefore, 0.1 g catalyst amount was chosen as an optimum catalyst amount for further study. Lower catalytic activity at low catalyst amount is due to the unavailability of sufficient active sites for isomerization reaction. As the amount of catalyst increased, availability of the active sites for double bond isomerization increases significantly. Therefore, higher conversion of methyl chavicol was observed on increasing the amount of cata-
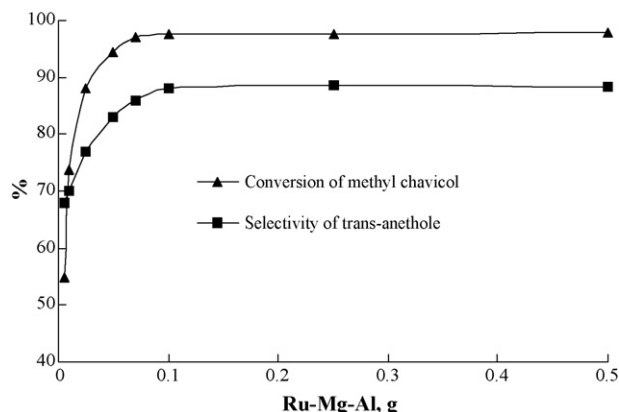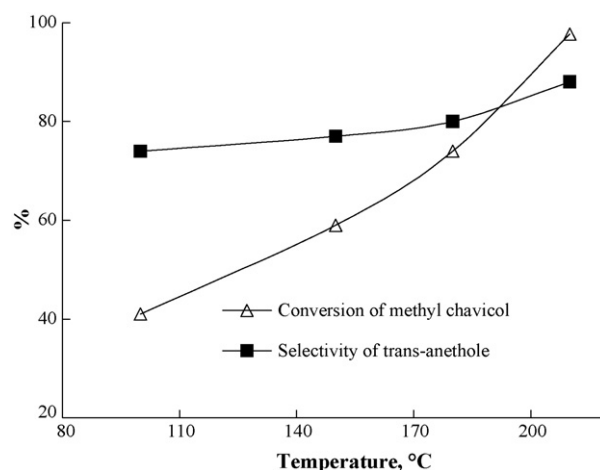

Fig. 5. Effect of reaction temperature on conversion of methyl chavicol and selectivity of *trans*-anethole using Ru–Mg–Al as a catalyst.

lyst. No conversion of methyl chavicol was observed in the absence of the catalyst.

The conversion of methyl chavicol was found to increase on increasing the reaction temperature (Fig. 5). At 100 °C, only 41% conversion of methyl chavicol was observed, which increased to 98% on increasing the reaction temperature to 210 °C. At lower temperature (100 °C), 74% selectivity of *trans* isomer was observed that increased to 88% at 210 °C.

3.3. Catalytic activity and reusability of various ruthenium impregnated catalysts

The catalytic activity and reusability of Ru–Mg–Al was compared with ruthenium impregnated catalysts namely, hydrotalcite [Ru–HT(3.5)], magnesium oxide (Ru–MgO), calcium oxide (Ru–CaO), silica (Ru–SiO$_2$) and alumina (Ru–Al$_2$O$_3$) (Table 2) by keeping similar ruthenium content at optimum reaction conditions. Pristine hydrotalcite, magnesium oxide, calcium oxide, silica and alumina were also used as catalysts to observe the role of ruthenium on their catalytic activity. Ruthenium incorporated in the brucite layer (Ru–Mg–Al) catalyst gave 98% conversion of methyl chavicol with 88% selectivity of *trans*-anethole within 2 h reaction time. Conversion and selectivity data for isomerization of methyl chavicol were observed to remain unchanged even after fourth run, confirming that the catalyst is reusable for the isomerization reaction without loss in its activity. The ruthenium metal complexes in homogeneous condition are well documented in the literature for isomerization of olefinic double bond [6]. The higher activity of Ru–Mg–Al catalyst as compared to HT(3.5) is due to presence of ruthenium in the brucite layer via isomorphic substitution of Mg or Al cations in the octahedral sheet is expected to be responsible for double bond isomerization reaction. Most of the active sites (hydroxyl groups coordinated to the ruthenium cations) are located at the outer surface of Ru–Mg–Al catalyst that makes it as an active and reusable catalyst. Another reason for higher activity of Ru–Mg–Al catalyst is the increased surface area of Ru–Mg–Al sample which favors the enhanced catalytic activity of the material as compared to the pristine hydrotalcite. No significant leaching of the ruthenium metal from the Ru–Mg–Al catalyst was observed in the ICP analysis of filtrate, due to the strong coordination of ruthenium cations in the hydrotalcite matrix as well as to the hydroxyl groups.

Ru–HT(3.5) showed comparable results, i.e. 97% conversion of methyl chavicol and 87% selectivity of *trans*-anethole, to the Ru–Mg–Al catalyst. However, conversion and selectivity were

Fig. 4. Catalytic activity of Ru–Mg–Al sample for isomerization of methyl chavicol to *trans*-anethole at varied amount of catalyst.

Table 2
Conversion and selectivity data of various ruthenium containing catalysts for isomerization of methyl chavicol to anethole.

Catalyst	Cycle	% Conversion	% Selectivity[a]	
			trans-Anethole	cis-Anethole
Ru–Mg–Al	First	98	88	12
	Second	98	88	12
	Third	98	88	12
	Fourth	97	87	13
Ru–HT(3.5)	First	97	87	13
	Second	95	85	15
	Third	92	81	19
	Fourth	88	76	24
HT(3.5)	First	20	80	20
	Second	4	81	19
Ru–MgO	First	97	85	15
	Second	97	82	18
	Third	89	78	22
	Fourth	84	71	29
MgO	First	24	72	28
	Second	6	70	30
Ru–CaO	First	62	90	10
	Second	15	87	13
	Third	7	85	15
	Fourth	3	84	16
CaO	First	15	75	25
	Second	2	65	35
Ru–SiO₂	First	98	79	21
	Second	85	73	27
	Third	77	62	38
	Fourth	70	59	41
SiO₂	First	5	45	55
	Second	–	–	–
Ru–Alumina	First	98	84	16
	Second	94	80	20
	Third	90	77	23
	Fourth	87	73	27
Alumina	First	10	72	28
	Second	2	–	–

[a] Reaction conditions: methyl chavicol = 5.0 g, catalyst = 0.5 g, temperature = 210 °C and reaction time = 2 h.

observed to decrease on reusability of the catalyst for the isomerization of methyl chavicol. For example, the conversion of methyl chavicol decreased from 97 to 88% with 76% selectivity for trans-anethole at the end of fourth cycle. Decrease in the conversion and selectivity is attributed to the leaching of ruthenium cations as 6% leaching was confirmed by ICP analysis from the surface of impregnated catalyst [Ru–HT(3.5)] during the catalytic reaction. 20% conversion of methyl chavicol was achieved with 80% selectivity of trans-anethole in 2 h using pristine hydrotalcite of Mg/Al molar ratio (3.5) [HT(3.5)] as a catalyst. On reuse of the catalyst, only 4% conversion of methyl chavicol was observed, which shows that the [HT(3.5)] is not a reusable catalyst in the present study for double bond isomerization reaction. On impregnation of ruthenium on MgO, the conversion of methyl chavicol increased from 24% (using pristine MgO as a catalyst) to 97% with 85% selectivity of trans isomer. The activity of Ru–MgO was observed to decrease on reusability experiments. At the end of fourth cycle, conversion of methyl chavicol decreased to 84% with 71% selectivity of trans-anethole. Among all ruthenium impregnated catalysts, Ru–CaO showed lower conversion of methyl chavicol (62%) with higher selectivity of trans-anethole (90%). The conversion was found to decrease very rapidly on the reusability experiments. Only 3% conversion of methyl chavicol was achieved at the end of fourth cycle, which is lower than the conversion observed by the use of pris-

tine CaO as a catalyst (15%). Rapid decrease in the conversion and selectivity data is due to the faster leaching of ruthenium metal. ICP analysis of Ru–CaO shows that the 86% of ruthenium was leached out from the catalyst after third cycle. Ruthenium impregnated silica and alumina also gave similar conversion of methyl chavicol (98%). However, higher selectivity of trans-anethole was observed with Ru–alumina (84%) as compared to Ru–SiO₂ (79%). On reusability of catalyst, rapid decrease in the conversion and selectivity was observed for Ru–SiO₂ as compared to Ru–alumina. The lower conversions of methyl chavicol, i.e. 5 and 10% were found when pristine SiO₂ and alumina, respectively, were used as catalysts. From the above data, Ru–Mg–Al was observed as a reusable catalyst for the double bond isomerization of methyl chavicol to trans-anethole. Except Ru–CaO, no significant effect of solid supports was observed on the conversion of methyl chavicol and selectivity of trans-anethole for isomerization of methyl chavicol. However, leaching of ruthenium from the solid supports has significant effect on the catalytic activity and reusability of ruthenium impregnated catalysts. Lower activity of Ru–CaO may be due to the lower surface area of catalyst.

3.4. Kinetic study for isomerization of methyl chavicol at optimum reaction conditions

For the kinetic study, reaction was carried out by taking 10 g methyl chavicol with 1 g Ru–Mg–Al as a catalyst at 210 °C reaction temperature. The kinetic profile for conversion of methyl chavicol and formation of cis- and trans-anethole with respect to time is shown in Fig. 6. 60% conversion of methyl chavicol was achieved within 2 min of reaction time that was observed to increase to 95% in 10 min. Most of the methyl chavicol was consumed for the formation of thermodynamically stable trans-anethole, however, small amount of cis-anethole was also observed at beginning of the reaction. As the reaction proceeded, formation of cis-anethole was also observed to increase. Initial rate of reaction for consumption of methyl chavicol was found to be $0.0026 \, \text{mol} \, \text{g}_{\text{cat}}^{-1} \, \text{min}^{-1}$ in the conversion range up to 25%. The initial rate of reaction for the formation of cis- and trans-anethole was calculated as 0.0003 and $0.0023 \, \text{mol} \, \text{g}_{\text{cat}}^{-1} \, \text{min}^{-1}$, respectively. The higher initial rate of reaction shows that the formation of trans isomer is more favorable in the present reaction conditions as compared to cis isomer.

3.5. Isomerization of other perfumery chemicals using Ru–Mg–Al as a catalyst

In view of observed higher catalytic activity and reusability of Ru–Mg–Al sample for isomerization of methyl chavicol, dou-
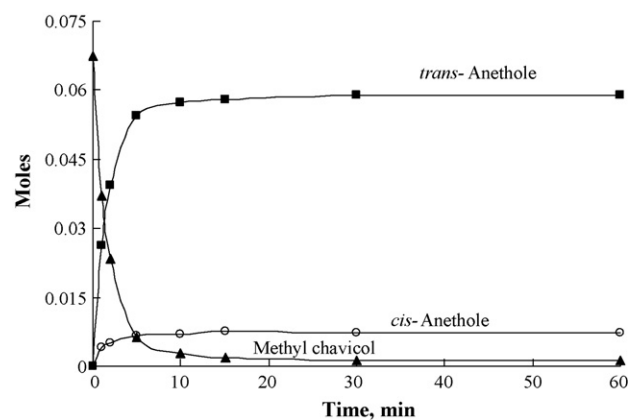

Fig. 6. Progress of double bond isomerization of methyl chavicol to anethole with respect to time using Ru–Mg–Al as a catalyst.

Table 3
Conversion and selectivity data for double bond isomerization of various chemicals with Ru–Mg–Al as a catalyst.

Run	Reactant	% Conversion[a]	% Selectivity	
			trans isomer	*cis* isomer
1	Methyl chavicol	98	88	12
2	Eugenol	94	89	11
3	Allylbenzene	96	88	12
4	Dimethoxy allylbenzene	92	88	12
5	Safrole	97	89	11
6	3-Carene	88	72	–

[a] Reaction conditions: reactant = 5.0 g, catalyst = 0.5 g, temperature = 210 °C and reaction time = 2 h.

Table 5
Effect of ruthenium content on catalytic activity of Ru–Mg–Al for double bond isomerization of methyl chavicol.

Run	wt% Ruthenium content in Ru–Mg–Al	% Conversion[a]	% Selectivity	
			trans isomer	*cis* isomer
1	0.3	61	89	11
2	0.5	79	89	11
3	1.0	98	88	12
4	1.5	100	88	12
5	5	100	80	14
7	10	100	73	17

[a] Reaction conditions: reactant = 5.0 g, Ru–Mg–Al = 0.5 g, temperature = 210 °C and reaction time = 2 h.

ble bond isomerization in other perfumery compounds such as, eugenol, allylbenzene, dimethoxy allylbenzene, safrole, 3-carene was studied using Ru–Mg–Al as a catalyst. 98% conversion of methyl chavicol with 88% selectivity of *trans*-anethole was observed within 2 h reaction time (Table 3). Double bond isomerization of eugenol showed 94% conversion of eugenol with 89% selectivity of *trans*-isoeugenol. Lower conversion of eugenol as compared to methyl chavicol could be attributed to the higher boiling point and viscosity of the reactant. The allylbenzene isomerization showed 96% conversion with 88% selectivity for *trans* isomer. In case of isomerization of dimethoxy allylbenzene, 92% conversion was observed. For isomerization of safrole, 97% conversion with 89% selectivity of *trans*-isosafrole was achieved. The data presented in this study for solvent free catalytic isomerization of safrole and eugenol is comparable with the results reported by Kishore et al., using hydrotalcite as a catalyst (substrate to catalyst ratio 2:1) in the presence of solvent, DMSO [9]. 88% conversion of 3-carene with 72% selectivity of 2-carene was observed using Ru–Mg–Al as a catalyst for isomerization of 3-carene. These data indicates that the Ru–Mg–Al is a highly active and reusable catalyst for double bond isomerization of variety of substrates related to the fine and perfumery chemicals.

3.6. Effect of activation of catalysts on their activity for isomerization of methyl chavicol

The catalytic activity of Ru–Mg–Al and pristine hydrotalcite of varied Mg/Al molar ratio was observed to decrease on activation at 450 °C for 4 h (Table 4). For example, conversion of methyl chavicol and selectivity of *trans*-anethole were observed to decrease from 98 to 48% and 88 to 80%, respectively, on activation of Ru–Mg–Al catalyst. With pristine hydrotalcite, the conversion of methyl chavicol was observed to increase on increasing the Mg/Al molar ratio of activated hydrotalcite from 2.0 to 3.5. For activated hydrotalcite of Mg/Al molar ratio 2.0, 8% conversion of methyl chavicol

was observed with 70% selectivity of *trans*-anethole in 10 h reaction time. The conversion increased to 20% with 80% selectivity of *trans*-anethole using activated hydrotalcite of Mg/Al molar ratio 3.5 as a catalyst. The conversion of methyl chavicol is achieved even in longer reaction time (10 h) when pristine hydrotalcite was used as a catalyst as compared to the Ru–Mg–Al (2 h) for double bond isomerization of methyl chavicol. As-synthesized hydrotalcite of varied Mg/Al molar ratio showed higher conversion and selectivity of *trans* isomer as compared to activated hydrotalcite as a catalyst. These results confirmed that the hydroxyl groups present in the hydrotalcite play an important role for the relocation of double bond. When the catalyst was calcined at 450 °C, the material converted into mixed oxides phase of higher surface area and strong basic in nature (rich in Lewis basic sites) as compared to the as-synthesized hydrotalcite (Brønsted basic sites) [21]. In case of hydrotalcite-based catalysts, the observed results in the present study clearly showed that the catalyst having strong (Lewis) basic sites is less active as compared to the catalyst rich in Brønsted basic sites (as-synthesized hydrotalcite).

The effect of ruthenium content on catalytic activity of Ru–Mg–Al for double bond isomerization of methyl chavicol was evaluated by varying the ruthenium content from 0.3 to 10% (by wt). At lower ruthenium loading (0.3%), 61% conversion of methyl chavicol was obtained which increased to 98% on increasing the amount of ruthenium to 1.0% in Ru–Mg–Al catalyst (Table 5). The conversion of methyl chavicol increased to 100% on increase in the ruthenium loading to 1.5%. The selectivity of *trans*-anethole was not observed to change significantly up to 1.5% ruthenium content in Ru–Mg–Al catalyst, however, selectivity of *trans*-anethole decreased significantly to 80% on increasing the ruthenium content to 5% which further decreased to 73% at 10% ruthenium content in Ru–Mg–Al catalyst. The decrease in the selectivity of *trans*-anethole at higher ruthenium content in catalyst is due to the formation of other side products.

Table 4
Isomerization of methyl chavicol to anethole using thermally activated catalysts[a].

Run	Reactant	Catalyst	% Conversion[b]	% Selectivity		T, h
				trans isomer	*cis* isomer	
1	Methyl chavicol	Ru–Mg–Al	48	80	20	2
2	Eugenol	Ru–Mg–Al	41	81	19	2
3	Safrole	Ru–Mg–Al	43	77	23	2
4	Allylbenzene	Ru–Mg–Al	40	79	21	2
5	3-Carene	Ru–Mg–Al	38	70	30	2
6	Methyl chavicol	HT(3.5)	20	80	20	10
7	Methyl chavicol	HT(3.0)	16	78	22	10
8	Methyl chavicol	HT(2.5)	14	74	26	10
9	Methyl chavicol	HT(2.0)	8	70	30	10

[a] Activated at 450 °C for 4 h.
[b] Reaction conditions: reactant = 5.0 g, catalyst = 0.5 g, temperature = 210 °C and reaction time = 2 h.

4. Conclusions

Ruthenium incorporated hydrotalcite (Ru–Mg–Al) was used as a catalyst for the isomerization of methyl chavicol, eugenol, safrole, allylbenzene, dimethoxy allylbenzene and 3-carene. Ru–Mg–Al showed excellent catalytic activity for isomerization reaction in shorter reaction time. For example, 98% conversion of methyl chavicol with 88% selectivity of *trans*-anethole was observed in 2 h reaction time. The activity of Ru–Mg–Al was compared with the other ruthenium impregnated catalysts such as, Ru–HT, Ru–MgO, Ru–CaO, Ru–SiO$_2$ and Ru–alumina. Ru–Mg–Al catalyst was recycled up to fourth cycle without significant loss in its activity. Other ruthenium impregnated catalyst also showed comparable activity but significant loss in the catalytic activity was observed on reuse of the catalysts for isomerization of methyl chavicol. Reaction temperature was observed to have a significant effect on conversion and selectivity of *trans* isomer. Conversion of methyl chavicol increased from 41 to 98% and selectivity of *trans*-anethole increased from 74 to 88% on increasing the temperature from 100 to 210 °C using Ru–Mg–Al as a catalyst. Kinetic study at optimum reaction conditions showed that 95% conversion of methyl chavicol was achieved within 10 min reaction time. The initial rate of reaction was calculated from the kinetic profile and found to be 0.0026 mol g_{cat}^{-1} min^{-1}.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.10.017.

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