

Catalytic isomerization of estragole to anethole over hydrotalcites and HT-like compounds

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Abstract

The liquid phase isomerization of estragole to anethole, an industrially important reaction, was carried out over catalysts belonging to the family of hydrotalcites (HTs) of general formula $M(II)M(III)-xHT$, where $M(II) = Mg, Ni, Co, Zn$ and Cu , and $M(III) = Al, Fe$ and Cr with varying $M(II)/M(III)$ atomic compositions (here represented as 'x'). Among various binary hydrotalcites investigated Mg and Ni offered maximum activity wherein $MgAl-4HT$ showed 99% conversion and $NiAl-4HT$ showed 87% conversion with a *cis:trans* ratio close to 15:85 at 200 °C at a substrate:catalyst mass ratio of 5:1. The other binary systems, $ZnAl-4HT$, $CoAl-4HT$ and $CuAl-4HT$ showed no conversion under similar reaction conditions. Among the trivalent metal ions studied, Al offered maximum activity followed by Fe and Cr and the activity trend was in line with the crystallinity of the samples. End members of the series, namely $Mg(OH)_2$ and $Al(OH)_3$, yielded no conversion, while materials crystallized as hydrotalcite (containing Mg and Al) showed pronounced activity, however varied with Mg/Al atomic ratio. Among the synthesis methodologies studied for $MgAl-4HT$, co-precipitation under low supersaturation offered maximum activity and solvent variation studies indicated that more polar solvents favored the reaction. The catalyst, $MgAl-4HT$, was reusable without significant loss in the activity up to three cycles. Variation of co-bivalent metal ions in $MgM(II)'Al-yz$ (where yz is $Mg:M(II)'$ atomic ratio and $M(II)' = Ni, Co, Zn, Cu, Mn$ and Fe) ternary hydrotalcites showed that the inclusion of Ni and Co in the HT framework resulted in synergism wherein $MgNiAl-31$ showed 98% conversion and $MgCoAl-31$ showed 88% conversion with *cis:trans* ratio close to 15:85 at 200 °C with a substrate:catalyst mass ratio of 10:1. In contrast, a sharp drop in the activity (<10%) was observed with other co-bivalent metal ions. A reaction mechanism involving hydroxyl groups of HT-like lattice is proposed for this reaction.

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1. Introduction

Isomerization of estragole (methyl chavicol) to the corresponding thermodynamically stable anethole (Scheme 1) is an important olefin isomerization reaction wherein the product finds application in alcoholic beverage industry and in oral hygiene products. Anethole occurs in nature as both *cis* and *trans* forms, wherein *trans*-isomer being more abundant. *t*-Anethole is a major component of several essential oils, including anise seed oil (80–90%), star anise oil (>90%) and sweet fennel oil (80%). Industrial sources of anethole have changed to address

an increasing demand. When demand was low, isolation from essential oils played a significant role as a commercial source. Increased demand led to isolation from crude sulfate terpentine (CST) or synthetic sources such as anisole [1,2]. Thach and Strauss [3] have carried out the isomerization of methyl chavicol in a microwave batch reactor under aqueous conditions using 0.2 M NaOH and obtained a conversion of 81% at 230 °C. Kameda and Yoneda [4] have reported homogeneous isomerization of estragole over $[RhH_2(Ph_2N_3)(PPh_3)_2]$ in dimethyl sulfoxide (DMSO) under hydrogen atmosphere (1 atm) at 30 °C. They found that the isomerization rate under hydrogen atmosphere was faster than that under nitrogen, and proposed that the active species was formed through the reaction of dihydridorhodium complex with hydrogen. However, most of these reactions involve a multi-step synthesis, carried out using stoichiometric or superstoichiometric reagents

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products were withdrawn using a syringe at definite time intervals and analyzed (using authentic samples) by gas chromatography (Shimadzu-14B, SE-30) using FID. Quantification of the products was done using 2-propanol as external standard. Identification of the products was also further verified using GC–MS (HP-5890-II GC connected to HP-5971 mass selective detector) as well as ^1H NMR (Bruker, Avance-200).

3. Results and discussion

3.1. Physicochemical studies

The chemical composition, lattice parameters and textural parameters of as-synthesized binary hydrotalcites have been already reported [12]. PXRD of these samples showed sharp and symmetric reflections at lower diffraction angles and broad asymmetric reflections at higher angles, characteristic of HT-like materials. Further evidence on the phase purity was ascertained from FT-IR whose spectra are given in Fig. 1. For all samples, infrared spectra are quite similar though some differences can be noticed in the intensity and the broadness of the bands. All spectra exhibited an intense broad band between 3800 and 3000 cm^{-1} which comprises the vibrations of physisorbed water [19,20], vibrations of structural OH^- groups [20], characteristic valency vibrations of $\text{OH}\cdots\text{OH}$ and/or characteristic stretching vibrations of $\text{CO}_3^{2-}\cdots\text{OH}^-$ in hydrotalcite [21]. A rather weak absorption at 1650–1620 cm^{-1} should be due to the deformation mode of interlayer water molecules [22]. An intense, sharp absorption band at 1360–1390 cm^{-1} is due to mode ν_3 anti-symmetric stretching of interlayer carbonate, shifted from its position in free CO_3^{2-} because of strong hydrogen bonding with hydroxyl sheets and H_2O molecules in the interlayer [21]. The presence of the band at 1504–1537 cm^{-1} , more clearly seen for MgCr-4HT (Fig. 1f), can be ascribed to a lowered carbonate symmetry (from D_{3h}) that activated the vibration mode ν_1 of CO_3^{2-} observed around 1080 cm^{-1} [23]. Bands observed between 800 and 400 cm^{-1} are attributed to the hydrotalcite lattice vibrations [24,25].

The adsorption–desorption isotherms of the samples (Fig. 1S, supplementary information) recorded at liquid nitrogen

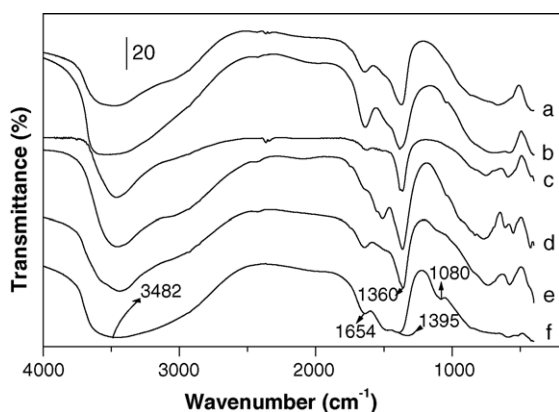


Fig. 1. FT-IR spectra of: (a) MgAl-4HT; (b) NiAl-4HT; (c) CoAl-4HT; (d) ZnAl-4HT; (e) MgFe-4HT; (f) MgCr-4HT.

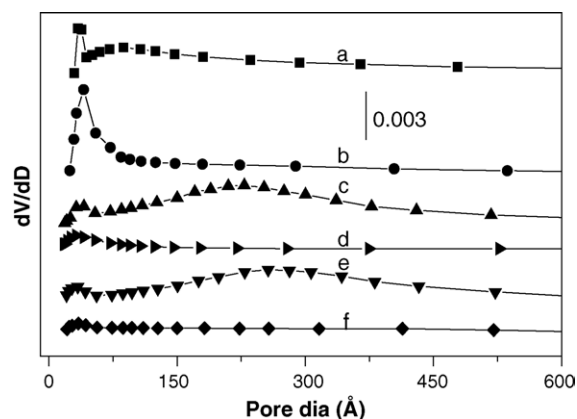


Fig. 2. BJH pore size distribution (desorption) traces of: (a) MgAl-4HT; (b) NiAl-4HT; (c) CoAl-4HT; (d) ZnAl-4HT; (e) MgFe-4HT; (f) MgCr-4HT.

temperature (-196°C) showed pattern typical of type IV isotherm according to IUPAC classification [26]. This represents a mesoporous adsorbent with no or a small amount of micropores and strong adsorbent–adsorbate interaction. Hysteresis loops were noted and are caused by the physical phenomenon of capillary condensation in mesopores. In most cases, the loop starts at a high relative pressure, which augments the mesoporous nature of these samples. The hysteresis loops are almost vertical and parallel over an appreciable range of p/p_0 and such shape of the loops suggests the presence of plate-like particles giving rise to slit-shaped pores [26]. The pore size distribution of the samples calculated according to Barrett et al. [27] from the results of the N_2 -desorption measurements, given in Fig. 2, pointed out significant variations in the distributions depending on the nature of metal ions in the HT-like lattice. For example, NiAl-4HT showed an intense and unimodal distribution with a peak maximum around 41 Å, while distribution traces of MgAl-4HT, MgFe-4HT and CoAl-4HT showed broad, bi-modal distribution of pores suggesting altered textural characteristics. Further, the contribution of pores in the lower mesoporous region (20–50 Å) significantly varied with the nature of metal ions present in the HT-like lattice. This is indeed reflected in specific surface areas and pore volumes of these samples [12]. To complement, scanning electron microscopic (SEM) studies were carried out for these materials in order to understand their morphological features. SEM micrographs of some of the samples are given in Fig. 3. A first look at the micrographs would indicate that all the samples possess platelet structures, however, with overlapping of such platelets occurs, thereby exhibiting a kind of spongy structure. However, extent of overlapping significantly varied with nature of metal ions thereby exhibiting varied sizes of agglomerated particles (MgAl-4HT: 1.5–3.5 μm ; MgFe-4HT: 0.2–0.7 μm). Such variations in orderliness of lattice, texture and morphology are expected to play a critical role in altering the reactivity of these materials for a catalytic reaction.

3.2. Isomerization of estragole

3.2.1. Influence of $M(\text{II})/M(\text{III})$ atomic composition

Table 1 summarizes the isomerization of estragole over MgAl binary hydrotalcites with varying Mg/Al atomic com-

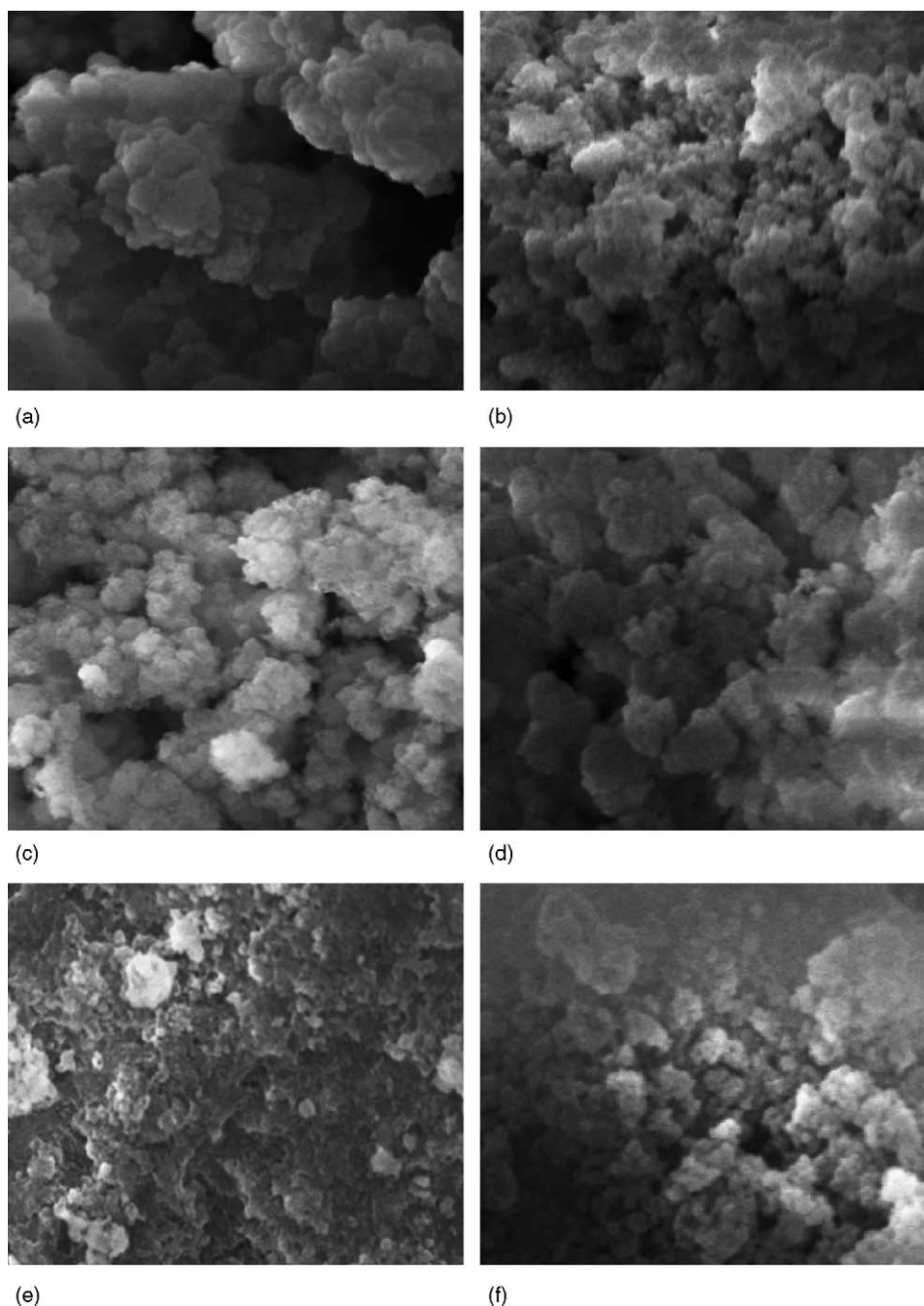


Fig. 3. Scanning electron micrographs of: (a) MgAl-4HT; (b) NiAl-4HT; (c) CoAl-4HT; (d) ZnAl-4HT; (e) MgFe-4HT; (f) MgCr-4HT (scale: 1 cm = 1 μ m).

positions. End members, namely $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$, are also included for comparison. Both end members yielded no conversion, while MgAl hydroxycarbonate crystallizing in HT-like network showed higher activity, however, the activity varied with Mg/Al atomic ratio. Activity variations indicated that the conversion increased with an increase in the ratio of Mg/Al up to 4.0 and a further increase in the ratio lowered the conversion. This could possibly be due to the variation in the basicity of the catalysts with varying Mg/Al atomic ratio. Among the catalysts studied, MgAl-4HT showed maximum conversion of 99% with a *cis:trans* ratio of around 14:86. *trans*-Isomer was formed

predominantly over all catalysts due to its better thermodynamic stability.

3.2.2. Influence of synthesis methodology

In literature, different methods have been reported for the synthesis of hydroxycarbonate-like materials [15]. Recently, hybrid syntheses wherein precipitation coupled with post-treatment employing microwave or ultrasound are attempted in an anticipation of obtaining varied physicochemical properties [28,29]. In our study, we have synthesized MgAl binary hydroxycarbonate with Mg/Al atomic ratio 4.0 (MgAl-4HT) by five different methods,

Table 1
Isomerization of estragole over MgAl hydrotalcites with different Mg/Al atomic compositions^a

Catalyst	Conversion (%)	Product distribution (%)	
		<i>cis</i>	<i>trans</i>
MgAl-2HT	31	13	87
MgAl-3HT	64	20	80
MgAl-4HT	99	14	86
MgAl-6HT	52	17	83
MgAl-8HT	29	14	86
MgAl-10HT	7	14	86
Mg(OH) ₂	n.c. ^b	–	–
Al(OH) ₃	n.c.	–	–
Blank	n.c.	–	–

^a Substrate: 0.5 g, solvent: DMF (20 ml), catalyst weight: 100 mg, reaction temperature/time: 200 °C/6 h.

^b No conversion.

namely sequential precipitation, co-precipitation, reversal addition, instantaneous addition and ultrasonication and their isomerization activity for estragole was compared. Experimental details of these synthesis methods are disclosed elsewhere [30]. The results are summarized in Table 2. It is clear from the table that among the methods studied, sample synthesized through co-precipitation showed maximum activity. The activity trend could be correlated with crystallinity of these materials, as evidenced from PXRD of these samples [12], wherein well crystalline sample, like that obtained through co-precipitation, showed maximum activity while samples with lesser long range ordering showed lower activity. These results are similar to that observed for isomerization of eugenol over these materials [12]. The higher crystallinity of the sample prepared through co-precipitation can be attributed to a facile particle growth. However, no regular correlation could be established between the activity and specific surface areas (Table 2) of these samples. Subsequently, all samples disclosed in this study mentioned below were synthesized by co-precipitation.

3.2.3. Influence of solvent

Table 3 summarizes the estragole isomerization activity in various solvents over MgAl-4HT. Although a direct correlation between the polarity of the solvent (as evidenced from their dielectric constants given in Table 3) with the activity could not be made, a general trend could be deduced wherein solvents with higher polarity such as dimethyl sulfoxide or

Table 3
Influence of solvent for isomerization of estragole over MgAl-4HT^a

Solvent	Dielectric constant	Conversion (%)	Product distribution (%)	
			<i>cis</i>	<i>trans</i>
DMF	38.2	97	12	88
DMSO	47.2	79	14	86
Acetonitrile	36.6	19	11	89
THF	7.5	10	10	90

^a Substrate: 0.5 g, solvent volume: 20 ml, catalyst weight: 100 mg, reaction temperature/time: 200 °C/6 h.

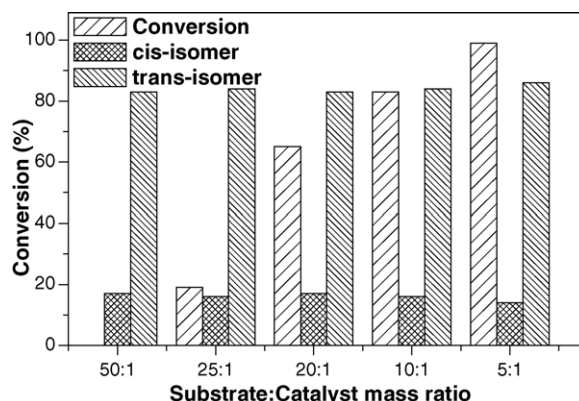


Fig. 4. Variation of substrate:catalyst mass ratio for isomerization of estragole over MgAl-4HT (substrate: 0.5 g; solvent: DMF (20 ml); reaction temperature/time: 200 °C/6 h).

N,N-dimethyl formamide (DMF) showed higher activity than the solvents with lower polarity such as THF. Highest conversion was noted for DMF and thus selected for further studies.

3.2.4. Influence of substrate:catalyst mass ratio

Fig. 4 shows the effect of substrate:catalyst mass ratio over MgAl-4HT. Conversion increased with an increase in catalyst mass. The *cis:trans* ratio also decreased (i.e. a decrease in *cis*-isomer) with an increase in conversion (i.e. at higher catalyst:substrate ratio). A maximum conversion of 99% in 6 h was observed with a substrate:catalyst mass ratio of 5:1 with a *cis:trans* ratio of 14:86 at 200 °C. To check the reusability of this catalyst, a fresh portion of estragole (0.5 g) along with solvent (DMF; 20 ml) was added to this reaction mixture and the reaction was continued. A conversion of around 85% was noted after

Table 2
Influence of synthesis methodology for MgAl-4HT on isomerization of estragole^a

Methodology	Mg/Al atomic ratio		Conversion (%)	Product distribution (%)		Surface area ^b
	Solution	Solid		<i>cis</i>	<i>trans</i>	
Co-precipitation	4.0	3.5	99	14	86	83
Ultrasonication	4.0	3.9	83	15	85	109
Sequential precipitation	4.0	3.8	80	15	85	78
Instantaneous addition	4.0	4.6	80	15	85	9
Reversal addition	4.0	4.0	66	15	85	26

^a Substrate: 0.5 g, solvent: DMF (20 ml), catalyst weight: 100 mg, reaction temperature/time: 200 °C/6 h.

^b Specific surface area in m²/g.

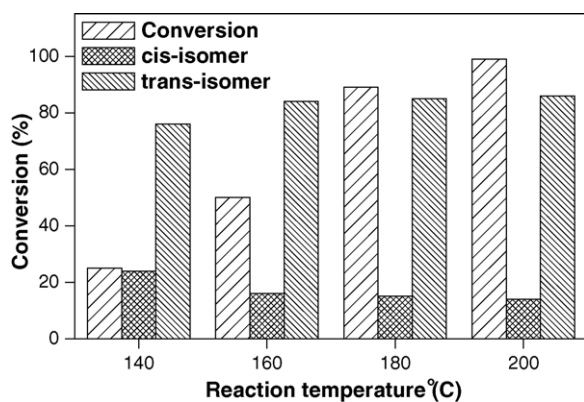


Fig. 5. Influence of reaction temperature on the conversion and selectivities of *cis*- and *trans*-anethole over MgAl-4HT (substrate: 0.5 g; solvent: DMF (20 ml); catalyst weight: 100 mg; reaction time: 6 h).

12 h of the reaction corroborating its potency to reuse. The slight decrease in the conversion could be due to decrease in catalyst concentration per unit volume of the reaction mixture. Further, when the catalyst was filtered after the reaction, washed (with water and finally with acetone to completely remove organics) and tested for isomerization, no significant drop in the conversion (~90% up to three cycles) was noted suggesting its promise for practical applications.

3.2.5. Influence of reaction temperature and time

Fig. 5 shows the isomerization activity of estragole over MgAl-4HT with substrate:catalyst mass ratio 5:1 in the temperature range 140–200 °C. The results showed that the catalytic activity increased with an increase in the reaction temperature. A gradual increase in the conversion was observed when the temperature was raised and a maximum conversion of 99% with *cis:trans* ratio 14:86 was observed at 200 °C. Hence, this temperature was selected for further studies. A progressive growth in the conversion of estragole was observed with reaction time wherein nearly 75% of the reaction occurred in 1 h and reached a maximum at 6 h as evidenced from Fig. 6. Observation of dual kinetic regimes for this reaction over these catalysts is a subject of further investigation.

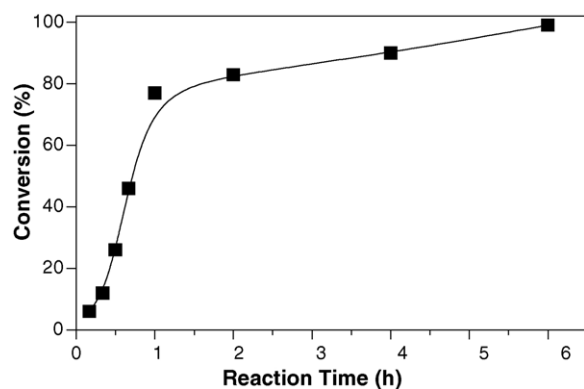


Fig. 6. Influence of reaction time on the conversion of estragole over MgAl-4HT (substrate: 0.5 g; solvent: DMF (20 ml); catalyst weight: 100 mg; reaction temperature: 200 °C).

Table 4

Isomerization activity of estragole over MgAl-4HT calcined at different temperatures in air for 5 h^a

Calcination temperature (°C)	Conversion (%)	Product distribution (%)	
		<i>cis</i>	<i>trans</i>
As-synthesized	97	12	88
200	27	20	80
400	0.3	–	100
600	0.2	–	100
800	0.1	–	100

^a Substrate: 0.5 g, solvent: DMF (20 ml), catalyst weight: 100 mg, reaction temperature/time: 200 °C/6 h.

3.2.6. Influence of calcination temperature

In an anticipation of finding better catalysts, MgAl-4HT was calcined at different temperatures (200, 400, 600 and 800 °C) in air for 6 h and tested for estragole isomerization. The temperatures were chosen based on thermoanalytical results. Although recent interest is in exploring the basic and/or redox properties of as-synthesized hydrotalcites for various catalytic transformations, larger reports are available on the utilization of calcined hydrotalcites as solid base catalysts for different base-catalyzed organic reactions such as condensation, dehydrogenation and isomerization [31,32]. Our studies indicated a sharp drop in the conversion of estragole for the calcined samples compared to as-synthesized samples irrespective of the calcination temperature (Table 4). The reason for such a drastic drop in the conversion is due to structural change wherein the destruction of layered structure occurs at higher temperatures forming mixed metal oxide. Significant difference in the activity between MgAl-4HT (97%) and the corresponding sample calcined externally at 200 °C for 6 h (27%) suggests the superiority of basic sites generated “in situ” for the former under our reaction conditions. This is evidenced by FT-IR measurements, given in Fig. 7, for MgAl-4HT calcined at different temperatures. The absorptions around 3450 cm⁻¹ of the OH group and 1380 cm⁻¹ of CO₃²⁻ group in the interlayer are reduced with an increase in the temperature of calcination along with variations in the spectra below 1000 cm⁻¹ corroborates the transformation of HT-like lattice to mixed metal oxide. The presence of water in the calcined

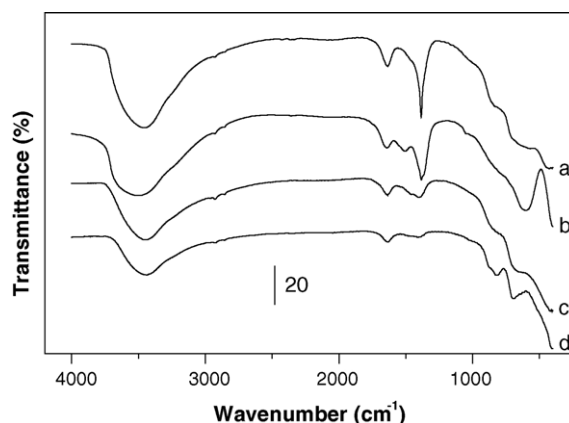
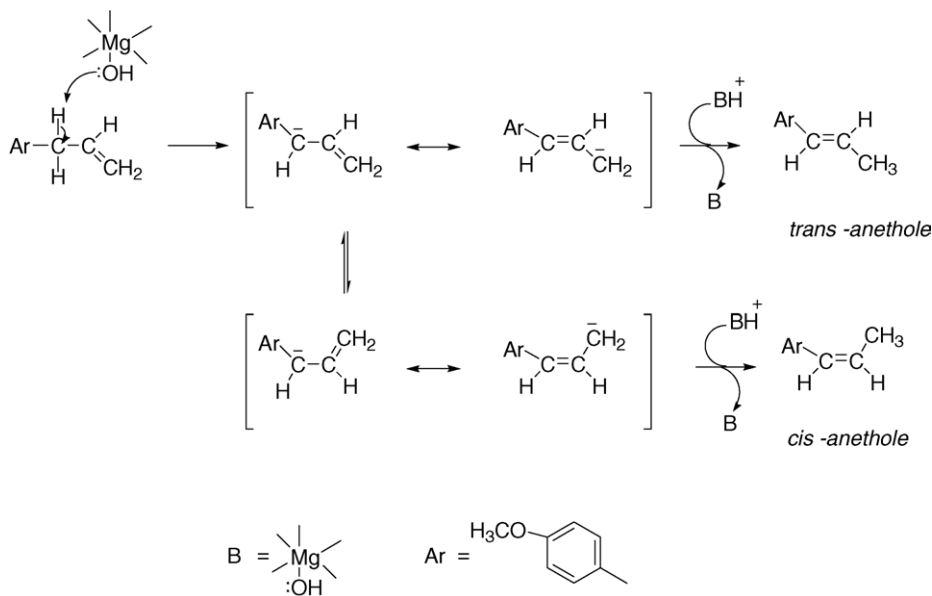


Fig. 7. FT-IR spectra of MgAl-4HT calcined at different temperatures for 5 h in air: (a) 200 °C; (b) 400 °C; (c) 600 °C; (d) 800 °C.



Scheme 2. Reaction pathway for isomerization of estragole over MgAl hydrotalcite.

samples (deformation mode at 1640 cm^{-1}) can be due to adsorption of water while handling the sample before measurements. Further, such inference is earlier substantiated by us using in situ PXRD measurements and TG-DTA studies [33]. In other words, one can say that strong Lewis basic sites (O^{2-}) derived from the calcination of hydrotalcites, may not be appropriate for enabling estragole isomerization while Bronsted basic hydroxyls (hydroxylated layered network) are the active centers, which abstract proton of methylene carbon in facilitating the isomerization. A probable mechanistic pathway for isomerization of estragole over MgAl binary hydrotalcite is depicted in Scheme 2.

3.2.7. Influence of bivalent metal ions

Various binary hydrotalcites of the general formula M(II)Al-4HT , where $\text{M(II)} = \text{Mg, Ni, Co, Cu}$ and Zn were screened for isomerization and the results are summarized in Table 5. Among the samples studied, magnesium and nickel offered high conversions (99 and 87%, respectively) at 200°C with a substrate:catalyst mass ratio of 5:1. Further, irrespective of metal ions the *trans*-isomer of anethole is the preferred product (around 85%) due for its thermodynamic stability. All the other bivalent metal ions showed no activity under similar reaction

conditions. This clearly suggests that the presence of appropriate basic sites in Mg and Ni systems, which assist in mediating the reaction. The observed high activity of nickel and magnesium systems can be attributed to the higher thermal stability of Ni and Mg systems, as deduced from second transformation temperature T_2 (334°C for NiAl-4HT and 403°C for MgAl-4HT) deduced from thermogravimetric profiles while rest of the binary samples structurally decomposed well below 250°C . In other words, prevalence of hydroxylated layered network is essential for facilitating estragole isomerization. Further, larger contribution of uniform pores in these samples (MgAl-4HT and NiAl-4HT) in $20\text{--}50\text{ \AA}$ region (Fig. 2) probably facilitates appropriate diffusion of molecules (reactant/products through intra/inter crystalline spaces) and in turn influences on the activity. We believe that the structural hydroxyl groups participate as Bronsted basic sites, preferably those present at the edges and surfaces of crystallites, which are accessible for the reactant molecules in enabling this reaction.

3.2.8. Influence of trivalent metal ion

In an endeavor to study the influence of trivalent cations, a series of hydrotalcites of general formula MgM(III)-4HT , where $\text{M(III)} = \text{Al, Fe}$ and Cr with Mg/M(III) atomic ratio of 4.0 were tested for isomerization of estragole. Among the catalysts studied, MgAl-4HT offered maximum conversion of 99% followed by Fe and Cr, which showed 37 and 8% conversion, respectively. A look at the conversion trend suggested a correlation with the crystallinity of the compounds wherein PXRD showed a maximum crystallinity for Al followed by Fe and Cr [12]. These results are further corroborated by FT-IR (Fig. 1) and SEM (Fig. 3) measurements wherein the former showed reduced symmetry of carbonate anions in the interlayers of MgFe-4HT and MgCr-4HT (and in turn on the long range ordering of the HT-like lattice) while the latter showed a larger average crystallite size of the particles for MgAl-4HT compared to MgFe-4HT and MgCr-4HT.

Table 5
Influence of bivalent metal ions in M(II)Al-4HT for estragole isomerization^a

Catalyst	Conversion (%)	Product distribution (%)	
		<i>cis</i>	<i>trans</i>
MgAl-4HT	99	14	86
NiAl-4HT	87	15	85
ZnAl-4HT	n.c. ^b	–	–
CuAl-4HT	n.c.	–	–
CoAl-4HT	n.c.	–	–

^a Substrate: 0.5 g, solvent: DMF (20 ml), catalyst weight: 100 mg, reaction temperature/time: $200^\circ\text{C}/6\text{ h}$.

^b No conversion.

Table 6
Isomerization of estragole over MgNiAl ternary hydroxalates^a

Catalyst	M(II)/Al ^b		Mg/Ni ^b		Conversion (%)	Product distribution (%)	
	Solution	Solid	Solution	Solid		<i>cis</i>	<i>trans</i>
MgNiAl-15	4.0	3.9	0.2	0.2	59	15	85
MgNiAl-13	4.0	4.5	0.3	0.3	73	14	86
MgNiAl-11	4.0	4.3	1.0	1.1	79	16	84
MgNiAl-31	4.0	4.3	3.0	2.9	98	15	85
MgNiAl-51	4.0	4.8	5.0	5.8	98	13	87
MgAl-4HT	4.0	3.5	–	–	83	16	84
NiAl-4HT	4.0	4.5	–	–	73	15	85

^a Substrate: 0.5 g, solvent: DMF (20 ml), catalyst weight: 50 mg, reaction temperature/time: 200 °C/6 h.

^b Atomic ratio.

3.2.9. Influence of co-bivalent metal ions

In order to understand the influence of co-cation on the physicochemical and catalytic properties of hydroxalates, we have partially substituted Mg by various bivalent metal ions in MgAl system. The selection of Mg and Al as bi- and trivalent cations in HT-like lattice were based on our results mentioned above, which showed high activity for estragole isomerization among various bivalent and trivalent metal ions screened. Table 6 summarizes the activity of MgNiAl ternary hydroxalates with varying Mg/Ni atomic compositions studied for estragole isomerization. For comparison, activities of MgAl-4HT and NiAl-4HT are also included in the table. Elemental analysis of these samples are also included in this table suggests a reasonable correspondence between the starting solutions and resulting solids substantiating the completion of precipitation. Phase purity was ascertained through powder X-ray diffraction (Fig. 2S) wherein pure HT-like phase was found in the entire composition range studied without co-crystallization of any discrete impurity phases. On all the catalysts anethole formed as a mixture of *cis*- and *trans*-isomers. Among the catalysts studied, MgNiAl-51 and MgNiAl-31 showed maximum conversion and MgNiAl-15 showed minimum conversion, clearly suggesting the influence of nickel concentration on the activity. A regular variation in the activity was noted with Mg/Ni composition, wherein conversion decreased with an increase in nickel content. A maximum conversion of 98% was noted for MgNiAl31 with a *cis:trans* ratio of around 13:87 using a substrate:catalyst mass ratio of 10:1. These results suggest that

co-presence of both Mg and Ni together in a HT-like lattice exhibit a co-operative phenomenon for such systems, thereby exhibiting enhanced activity compared to independent binary systems. Recently, Rives et al. [34] demonstrated the operation of such synergism for Co and Ni containing ternary hydroxalates for hydroxylation of phenol. In an extension, to see the influence of other co-bivalent metal ions on MgAl system, we have synthesized MgM(II)'Al ternary systems, where M(II)' = Zn, Co, Cu, Fe and Mn with Mg/M(II)' atomic ratio of 3.0 (the ratio was chosen based on MgNiAl ternary system). PXRD of these samples showed (Fig. 3S) single phase diffraction pattern characteristic of HT-like phase (JCPDS: 41-1428) with varying crystallinity depending on the nature of co-bivalent metal ions present in the lattice wherein nickel showed the maximum crystallinity based on both basal and *ab* plane reflections. All catalysts containing other co-bivalent metal ions showed a sharp drop in the conversion, except for MgCoAl-31 (which showed a conversion of 88% with *cis:trans* ratio 16:84) under similar experimental conditions (Table 7). Such a decrease in the activity even upon minimal incorporation of inactive metal ions in MgAl layered lattice would suggest a strong negative influence of these metal ions in altering the basic characteristic of the hydroxyl groups, and in turn on the activity.

3.2.10. Influence of alkali metal ions and ruthenium loading

Many base-catalyzed organic transformations have been promoted by impregnating alkali metal ions especially on zeolites

Table 7
Isomerization of estragole over MgM(II)'Al ternary hydroxalates^a

Catalyst	(Mg + M(II)')/Al ^b		Mg/M(II)' ^b		Conversion (%)	Product distribution (%)	
	Solution	Solid	Solution	Solid		<i>cis</i>	<i>trans</i>
MgNiAl-31	4.0	4.3	3.0	2.9	98	15	85
MgCoAl-31	4.0	4.1	3.0	2.7	88	16	84
MgZnAl-31	4.0	4.2	3.0	2.7	8	16	84
MgCuAl-31	4.0	4.4	3.0	2.5	3	33	67
MgMnAl-31	4.0	4.4	3.0	3.6	4	25	75
MgFeAl-31	4.0	4.4	3.0	3.6	2	30	70

^a Substrate: 0.5 g, solvent: DMF (20 ml), catalyst weight: 50 mg, reaction temperature/time: 200 °C/6 h.

^b Atomic ratio.

through ion-exchange [35]. Recently, Kaneda et al. [36] have reported an increase in the activity for heterogeneous oxidation of allylic and benzylic alcohols for MgAl hydrotalcite by incorporating ruthenium. In an anticipation of complementing these studies, we had taken an initiative of incorporating alkali metal ions (mainly Cs⁺ using cesium acetate) or ruthenium (as Ru³⁺ using RuCl₃·3H₂O) over as-synthesized MgAl-4HT through impregnation (at room temperature for 6 h, aged at 65 °C for 12 h and dried at 110 °C for 6 h). The results evidenced that incorporation of ruthenium as well as of alkali metal ions improved the conversion compared to as-synthesized hydrotalcite. A conversion of 98% with a *cis:trans* ratio of 13:87 was noted for 2.5% Ru-incorporated hydrotalcite (ICP analysis showed a loading of 1.8% of Ru) against 83% conversion (*cis:trans* ratio of 16:84) for as-synthesized MgAl-4HT with a substrate:catalyst mass ratio of 10:1 under identical reaction conditions. In addition, samples with varying Ru content (1 and 0.5% Ru) were prepared and tested for estragole isomerization. The activity studies concluded that the amount of introduced ruthenium could be lowered to as low as 0.5% with out a marked variation in the estragole conversion and we propose that Ru³⁺ on the surface of hydrotalcite play a role in augmenting the catalytic behavior. Similarly, conversion also improved with alkali metal ion doping, wherein 5% Cs incorporated MgAl-4HT showed a conversion of 96% (against 83% for MgAl-4HT) with *cis:trans* ratio of 16:84 at 200 °C.

4. Conclusions

Isomerization of estragole to anethole was carried out over different series of hydrotalcites of general formula M(II)M(III)-*x*HT, where M(II) = Mg, Ni, Co, Cu and Zn, and M(III) = Al, Fe and Cr with different metal ion combinations and concentrations. Among various binary hydrotalcites studied with Al as trivalent cation, Mg and Ni showed maximum activity, while all the other bivalent metal ions showed no activity. Thermal stability and structural integrity of layered lattice are considered to be indispensable for enabling this reaction. Trivalent metal ion variation revealed a maximum activity for Al, followed by Fe and Cr, and a direct correlation was noted between the activity and the crystallinity of these solids. Solvents with higher polarity favored the reaction. Activity of calcined hydrotalcite (MgAl-4HT) was lower than the as-synthesized hydrotalcite irrespective of calcination temperature ascertained the importance of structural OH groups of HT-like lattice. Synergism was noted when highly active Mg and Ni were present together in the layered lattice as ternary hydrotalcite. MgNiAl-31 showed 98% conversion of estragole with a *cis:trans* ratio of around 15:85 using substrate:catalyst mass ratio of 10:1 at 200 °C. Minimal incorporation of inactive bivalent metal ions such as Cu, Zn and Mn in MgM(II)'Al ternary systems sharply decreased the isomerization activity (<10%) suggesting their strong negative influence on the basic characteristics of structural hydroxyl groups. Incorporation of ruthenium or cesium in MgAl-4HT enhanced the conversion of estragole. Bronsted basic hydroxyl groups attached to Mg²⁺

are proposed as active centers involved in this isomerization reaction.

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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.2005.08.049.

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