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Double bond migration of eugenol to isoeugenol over as-synthesized hydrotalcites and their modified forms

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Abstract

Double bond migration of eugenol to isoeugenol was carried out over as-synthesized hydrotalcites and their modified forms. The catalysts of general formula M(II)M(III)-*x*HT with carbonate as interlayer anion were synthesized by a co-precipitation method where M(II) = Mg, Ni, Co, Zn, Cu and M(III) = Al, Cr, Fe, La, V with varying M(II)/M(III) atomic compositions (here represented as '*x*'). The synthesized catalysts were tested for the reaction. Among various binary hydrotalcites investigated, Mg and Ni offered maximum activity, wherein MgAl-4HT showed nearly 73% conversion and NiAl-4HT showed 75% conversion with 15:85 *cis*:*trans* ratio at 200 °C with a substrate:catalyst mass ratio of 2:1. The other binary systems showed poor activity (less than 5%) under similar reaction conditions. The preservation of HT-like lattice is presumed to be crucial for this reaction, as evidenced from "in situ" powder X-ray diffraction (PXRD) and thermogravimetric (TG) analysis measurements. Variation in the trivalent metal ions indicated a maximum activity for Al, followed by Fe and Cr, in accordance with the crystallinity. A co-operative phenomenon was noted when both Mg and Ni were present together in a ternary MgNiAl-HT, however the activity varied with Mg/Ni atomic composition. Solvent variation studies indicated that more polar solvents favored the reaction. Significant promotional influence in the activity was noted with alkali and ruthenium impregnation on MgAl-4HT, wherein maximum activity was showed by catalysts modified with Cs (among the alkali metal ions studied) and higher content of ruthenium. Comparison of the activity with conventional bases such as KOH and KOBu^t revealed a superior performance of HT-based catalysts, although conventional bases had been used under stoichiometrically excess conditions (around 9% conversion for KOH with 1:10 and 5% conversion for KOBu^t with 1:3 substrate:catalyst mole ratio). The good performances of these catalysts encouraged further studies. A reaction mechanism involving the hydroxyl group of HT-like lattice is proposed for this isomerization reaction.

Keywords: Isomerization of eugenol; Crystallinity; "In situ" powder X-ray diffraction; HT-like lattice; Ru-incorporation; Alkali-doped hydrotalcite; Synergism

1. Introduction

Eugenol is isomerized to its corresponding alkenyl alkoxy benzene, isoeugenol, wherein the double bond in the alkenyl group migrates to a position conjugated with the benzene ring (Scheme 1). The product finds application in pharmaceuticals and in a wide variety of blossom compositions in fragrances [1,2]. Isomerization of eugenol is generally carried out in a homogenous medium using KOH in alcoholic solutions (most often in higher alcohols) at high temperatures [3]. Loupy and Thach [4] have attained quantitative yields when they used KOH or KOBu^t (2.2 mol equiv.) as catalyst in the presence of a phase transfer agent, Aliquat 336, under solvent-free conditions. Subsequently, they have also tested the effect of several additives under similar reaction conditions and achieved 90% yield with pyridine as an additive at 150 °C. Recently, Thach and Strauss [5] have carried out the isomerization of eugenol in a microwave batch reactor under aqueous conditions using 0.4 M NaOH; they obtained 73% conversion at 200 °C in 15 min. However, in all these cases, the amount of base employed was 10–20 times (w/w ratio) more than the substrate. In the literature, an alternative approach is described, wherein complexes of group VIII elements are employed for this reaction [6,7]. Kameda and Yoneda [8] have reported homogeneous isomerization of

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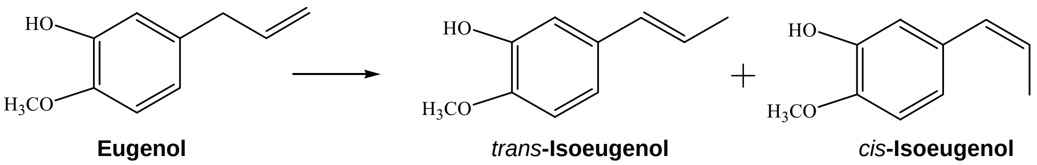


Scheme 1. Isomerization of eugenol to isoeugenol.

eugenol 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 atmosphere, and proposed that the active species was formed through the reaction of dihydridorhodium complex with hydrogen. Replacement of liquid bases by solid bases is a topic of recent interest, in view of cleaner environment [9–11]. Few reports are available on this transformation over solid catalysts under heterogeneous conditions. Sokolskii and Trukhachova [12] have studied isomerization of eugenol over palladium on alumina (5% Pd) catalyst in the liquid phase; they concluded that the activity and selectivity depended on the sequence of addition of reagents or salt in the catalytic system. Radhakrishna et al. [13] have carried out isomerization of eugenol on KF on neutral alumina in dry ethylene glycol and obtained around 78% yield at 200 °C. Very recently, Ramishvili et al. [14] have carried out isomerization of eugenol over various zeolites like Y, beta and mordenite, and obtained conversions of around 70–90% in helium or hydrogen. Parallel reactions such as hydrogenation, condensation or oxidation were noted when the reaction was done under hydrogen or with metal modification of these zeolites. Among different solid base catalysts disclosed in the literature, hydrotalcite-like compounds are one of the promising materials. They have been explored for several base-catalyzed reactions such as aldol condensation [15], double bond isomerization of alkene [16] and dehydrogenation of 2-propanol [17]. Structurally, they are layered materials with the general formula $[M(II)_{1-x}M(III)_x(OH)_2][A^{n-}_{x/n}] \cdot mH_2O$, where M(II) and M(III) are divalent and trivalent cations, A^{n-} is the interlayer anion and x can generally have the values between 0.1 and 0.33 [18]. Very recently, we have presented our first results on isomerization of eugenol and safrole over MgAl binary hydrotalcites [19]. It is also known in the chemistry of hydrotalcites [20,21] that, changing the nature of the cations in the layers, M^{2+}/M^{3+} ratio, nature of the compensating anions or activation methodology can modify the acid–base properties of these catalysts.

The present paper explains a detailed investigation on isomerization of eugenol over various M(II)M(III) hydrotalcite-like compounds, where M(II) = Mg, Ni, Co, Cu, Zn; M(III) = Al, Fe, Cr, V, La with carbonate as interlayer anion and varying M(II)/M(III) atomic compositions. An attempt has also been made to correlate the activity with structural properties.

2. Experimental

2.1. Sample preparation

The samples, unless specifically mentioned, were largely prepared by co-precipitation under low supersaturation. In this method, two solutions, namely, solution (A) containing the desired amount of metal nitrates and solution (B) having precipitating agents (i.e. NaOH and Na_2CO_3) were added slowly (1 ml/min) and simultaneously in a four-necked round-bottomed flask fitted with a pH electrode for maintaining the pH around 9–10 during addition under vigorous stirring at room temperature. The addition took ca. 90 min and the final pH was adjusted to 10 by adding a few drops of precipitant solution. The samples were aged in the mother liquor at 65 °C for 18 h, filtered, washed (until total absence of nitrates and sodium in the washing liquids) and dried in an air oven at 110 °C for 12 h. In most of the cases, the atomic ratio between the divalent and trivalent cations was maintained around 4.0, while in ternary systems the bivalent:cobivalent atomic ratio was varied between 1:0 and 0:1. Consequently, the samples here are named either as M(II)M(III)-*x*HT where *x* stands for M(II)/M(III) atomic ratio for binary systems or as M(II)M(II)’M(III)-*yz*HT, where *yz* stands for the nominal M(II):M(II)’ atomic ratio for ternary systems.

2.2. Techniques

Elemental chemical analysis of these samples was carried out by both conventional wet chemical methods and atomic absorption.

Powder X-ray diffraction (PXRD) (both ex situ and in situ) was carried out on a Philips X’Pert MPD system connected to an Anton-Paar high temperature XRK assembly using Cu Kα radiation. In situ measurements were carried out by mounting the sample in a high temperature cell, which was heated at 2.5 °C/min in steps of 25 °C and stabilized for 10 min before measurements. The operating voltage and current were 40 kV and 40 mA, respectively. The step size was 0.05° with a step time of 1 s. Identification of the crystalline phases was made by comparison with the JCPDS files [22].

FT-IR spectra were recorded in a Perkin-Elmer FT1730 instrument, using KBr pellets; 100 spectra (recorded with a nominal resolution of $4\,cm^{-1}$) were accumulated and averaged to improve the signal-to-noise ratio.

Thermogravimetric (TG) analysis was carried out in a Mettler TGA/SDTA 851^e and the data were processed using Star^e software, in flowing nitrogen or argon (flow rate, 50 ml/min), at a heating rate of 10 °C/min.

Specific surface area and pore size analysis of the samples were measured by nitrogen adsorption at −196 °C using a sorptometer (ASAP-2010, Micromeritics). The samples were degassed at 120 °C for 4 h prior to measurements and the data were analyzed using published software [23].

2.3. *Isomerization of eugenol*

Isomerization of eugenol was conducted in a batch reactor (50 ml), wherein the substrate, solvent and catalyst were charged all at once and raised to the reaction temperature. The products were withdrawn using a syringe at definite time intervals and analyzed (using authentic samples) by gas chromatography (Shimadzu-14B, OV-17) 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 ^{1}H-NMR (Bruker, Avance-200).

3. Results and discussion

3.1. *Physicochemical studies*

The chemical composition, lattice parameters and textural parameters of as-synthesized samples are given in Table 1. Elemental analysis of these samples showed a reasonable agreement between the solution M(II)/M(III) atomic ratios and those obtained for solids, suggesting completion of precipitation. However, deviations noted in the case of MgFe-4HT are probably due to incomplete precipitation, which is inherent for iron-containing systems [24]. Powder X-ray diffraction of these samples showed sharp and symmetric reflections at lower diffraction angles and broad asymmetric reflections at higher angles, characteristic of hydrotalcite-like layered materials. A representative diffraction profile of some of the samples synthesized is presented in Fig. 1. MgAl-4HT and MgFe-4HT showed patterns characteristic of synthetic hydrotalcite (JCPDS 41–1428), wherein aluminum showed maximum crystallinity, while MgCr-4HT showed a diffuse pattern with broad reflections; however, the position of the peak maximum is in correspondence with that of hydrotalcite. Among various bivalent metal ions studied, except for copper (which showed reflections of CuO along with HT-like phase), all of them showed a single-phase characteristic of hydrotalcite. The lattice parameters '*a*' and '*c*' calculated for these samples varied in accordance with the ionic radii of the metal ions present in the HT-like lattice. Among various bivalent metal ions screened, the crystallinity (as deduced from (0 0 3) and (1 1 0) reflections) followed the trend: Mg > Ni > Co > Cu. The differences in specific surface area and pore volume suggest that the textural properties are influenced with a variation in the nature of metal ions of the HT-like lattice.

Table 1
Physicochemical properties of the samples synthesized

Catalyst	Atomic ratio		Lattice parameters (Å)		Surface area (m^2/g)	Pore volume (cm^3/g)
	Solution	Solid	*a*	*c*		
MgAl-4HT	4.0	3.5	3.07	24.41	83	0.47
MgFe-4HT	4.0	2.4	3.03	22.80	105	0.59
MgCr-4HT	4.0	3.9	3.06	24.52	80	0.41
NiAl-4HT	4.0	4.5	3.05	23.81	125	0.45
CuAl-4HT	4.0	5.1	3.09	22.54	29	0.22
CoAl-4HT	4.0	4.7	3.01	23.10	117	0.81
ZnAl-4HT	4.0	4.9	3.08	23.29	44	0.27

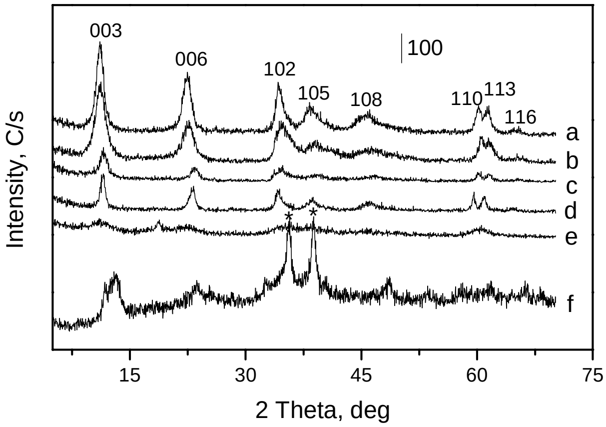


Fig. 1. Powder X-ray diffraction pattern of: (a) MgAl-4HT; (b) NiAl-4HT; (c) CoAl-4HT; (d) MgFe-4HT; (e) MgCr-4HT; (f) CuAl-4HT (HT—pattern in correspondence with synthetic hydrotalcite JCPDS: 41–1428; ⋆ —CuO, JCPDS: 5–0661).

3.2. *Isomerisation of eugenol*

3.2.1. *Influence of synthesis methodology*

In the literature, different methods have been reported for the synthesis of hydrotalcite-like materials [18]. Recently, hybrid synthesis, wherein precipitation coupled with post-treatment employing microwave or ultrasound, are attempted in an anticipation of obtaining varied physicochemical properties [25,26]. In our study, we have synthesized MgAl binary hydrotalcite with Mg/Al atomic ratio 4.0 (MgAl-4HT) by five different methods: namely, sequential precipitation, co-precipitation, reversal addition, instantaneous addition and ultrasonication. The isomerization activity values for eugenol were compared. Experimental details of these synthesis methods are disclosed elsewhere [27]. The results are summarized in Table 2. It is clear from the table that, among the methods studied, the sample synthesized through co-precipitation showed maximum activity. In all cases, isoeugenol as *cis*- and *trans*-isomers were the only products formed and no other products were detected

Table 2
Influence of synthesis methodology for MgAl-4HT on isomerization of eugenol[a]

Catalyst	Conversion (%)	Product distribution (%)		Surface area (m^2/g)
		Cis-isomer	*Trans*-isomer	
Sequential precipitation	40	25	75	78
Co-precipitation	73	16	84	83
Reversal addition	21	29	71	26
Instantaneous addition	41	27	73	9
Ultrasonication	45	25	75	109

[a] Substrate:eugenol (0.5 g); solvent: DMF (20 ml); catalyst weight: 250 mg; reaction temperature/time: 200 °C/6 h.

by GC analysis. The activity trend could be correlated with the crystallinity of these materials (PXRD patterns of these samples are shown in Fig. 2), wherein perfectly crystalline samples, like those obtained through co-precipitation, showed maximum activity while samples with lesser long range ordering showed lower activity. No regular correlation was noted between the activity and specific surface areas (Table 2) of these samples. Subsequently, all samples described in this study were synthesized by co-precipitation.

3.2.2. *Influence of solvent*

Table 3 summarizes the eugenol 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) [28] with the activity could not be made, a general trend could be deduced, wherein solvents with higher polarity such as dimethyl sulfoxide (DMSO) or *N*,*N*-dimethyl formamide (DMF) showed higher activity than the solvents with lower polarity such as tetrahydrofuran (THF) or toluene. However, it is quite surprising that high boiling hydroxylated solvents such as glycerol and glycol did not result in significant conversion under our reaction conditions. This is in contrast to the results of Salmario et al. [29] who claimed higher activity in glycol over KOH. We presume that there could be some lattice expansion of these materials in these solvents, which are known for their swelling abilities for layered compounds, causing some structural distortion, thereby resulting in poor activity. In addition, no significant variation in the conversion of eugenol was noted with the variation in the volume of solvent (5–30 ml). Highest conversion was observed for DMF and DMF was thus selected for further studies.

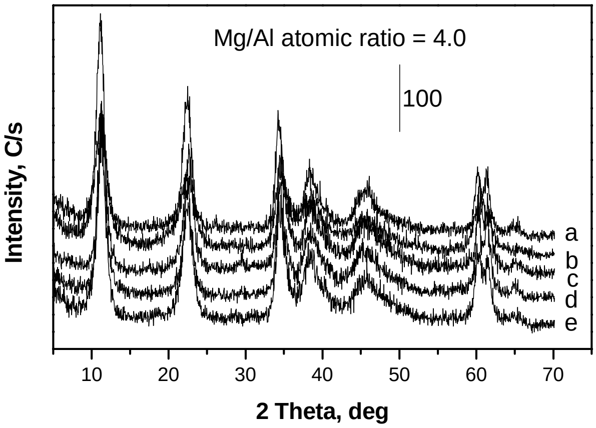


Fig. 2. PXRD patterns of: (a) MgAl-COP-4HT; (b) MgAl-SEQ-4HT; (c) MgAl-REV-4HT; (d) MgAl-INS-4HT; (e) MgAl-ULS-4HT.

Table 3
Influence of solvent for isomerization of eugenol over MgAl-4HT[a]

Solvent	Dielectric constant	Conversion (%)	Product distribution (%)	
			Cis-isomer	*Trans*-isomer
DMF	38.3	73	16	84
DMSO	47.2	47	23	77
2-Butanone	15.1	26	4	96
Tetrahydrofuran (THF)	11.6	6	17	83
Toluene	2.4	16	–	100
Glycerol	46.5	–	–	–
Glycol	41.4	–	–	–

[a] Reaction parameters as given in Table 2; solvent volume: 20 ml.

3.2.3. *Influence of bivalent metal ions*

Various binary hydrotalcites of the general formula M(II)Al-4HT, where M(II) = Mg, Ni, Co, Cu and Zn were screened for isomerization; the results are summarized in Table 4. Among these samples, magnesium and nickel offered maximum activity exhibiting around 75% conversion at 200 °C with a substrate:catalyst mass ratio of 2:1. Further, the *trans*-isomer of isoeugenol predominates in the product (around 85%), known for its thermodynamic stability. All the other bivalent metal ions showed poor activity (<5% conversion) under similar reaction conditions. This clearly suggests that the presence of appropriate basic sites in Mg and Ni systems helps in mediating the reaction. No significant difference in the activity was noted between Mg and Ni systems, irrespective of the variation in substrate:catalyst ratios. However, if one were to normalize the activity with specific surface area, MgAl-4HT was more active than NiAl-4HT. Furthermore, influence of reaction time studies for these catalysts indicated a progressive increase in the conversion with time and reached a maximum conversion level at 6 h while a

Table 4
Influence of bivalent metal ions in M(II)Al-4HT for eugenol isomerization[a]

Catalyst	Conversion (%)	Product distribution (%)	
		Cis-isomer	*Trans*-isomer
MgAl-4HT	73	16	84
NiAl-4HT	75	15	85
ZnAl-4HT	6	–	100
CuAl-4HT	–	–	–
CoAl-4HT	–	–	–

[a] Reaction parameters as given in Table 2.

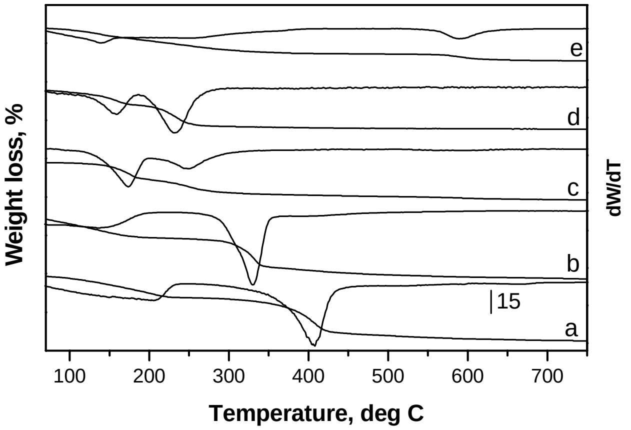


Fig. 3. TG–DTG curves of: (a) MgAl-4HT; (b) NiAl-4HT; (c) ZnAl-4HT; (d) CoAl-4HT; (e) CuAl-4HT.

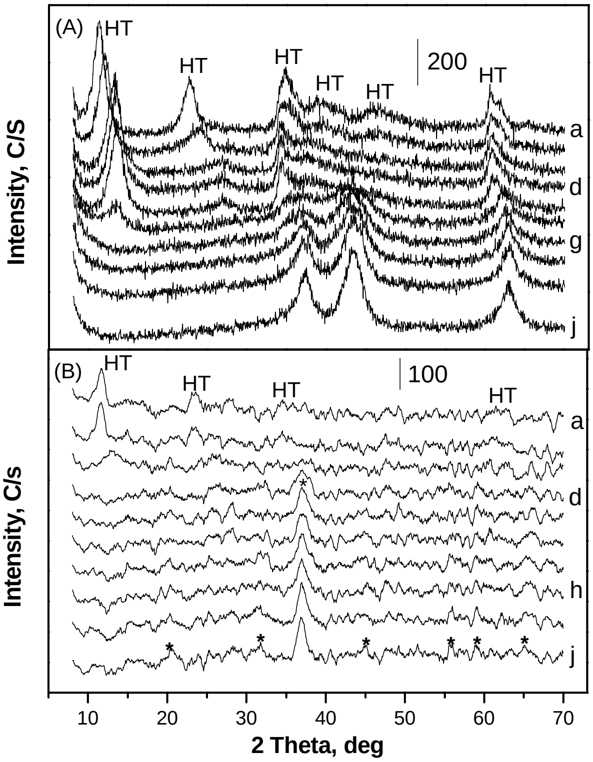


Fig. 4. In situ PXRD patterns of: (A) NiAl-4HT and (B) CoAl-4HT calcined at (a) 50, (b) 100, (c) 150, (d) 200, (e) 225, (f) 275, (g) 325, (h) 350, (i) 400 and (j) 450 °C (HT—hydrotalcite; ⋆ -spinel; ●-NiO).

further increase in the time did not significantly alter the conversion, suggesting the non-occurrence of interconversion or continuous reactions. The observed high activity for nickel and magnesium systems can be explained as follows.

Fig. 3 shows the TG–DTG patterns of all binary hydrotalcites synthesized. Generally, these samples show weight losses in two temperature windows, namely around 100–225 °C and between 200 and 450 °C, depending on the nature of the metal ion present in HT-like lattice. The first transformation is attributed to removal of intercalated water molecules, while the second loss is due to dehydroxylation of structural hydroxyls with concomitant decarbonation, resulting in destruction of the layered lattice [30]. It is clear from the figure that, other than Ni and Mg systems which showed higher thermal stability, as deduced from second transformation temperature T_2 (304 °C for NiAl-4HT and 403 °C for MgAl-4HT), all the samples structurally decomposed well below 250 °C. In other words, retention of structural integrity of HT-like lattice is one of the essential prerequisites for this reaction. We believe that the structural hydroxyl groups participate as Bronsted basic sites, preferably those present at the edges and surface, which are accessible for the reactant molecules. To compliment our results, we had done “in situ” powder X-ray diffraction and representative thermal evolution profiles of NiAl-4HT and CoAl-4HT are given in Fig. 4A and B. In the case of NiAl-4HT, with an increasing temperature both d_{003} reflection and d_{006} reflection (characteristic of interlayer ‘z’ direction) dropped in intensity and shifted to higher diffraction angles as well. The decrease in the intensity is attributed to decrease in the long range ordering, while the shift is attributed to partial removal of water molecules, resulting in shrinking of interplanar spacing [31]. The observation noted for CoAl-4HT was similar. However, a closer look at the spectra would indicate that the layered lattice (as reflected from the presence of both basal and ‘ab’ plane reflections observed around $2\theta = 60°$), although disordered, was present until 275 °C (Fig. 4A, spectra f) for NiAl-4HT and showed a diffuse pattern similar to NiO with a further increase in the calcination temperature (Fig. 4A, spectra g–j). However, in the case of CoAl-4HT, the layered lattice prevailed only upto 150 °C (Fig. 4B, spectra c) while diffuse spinel (peaks corresponding to spinel phase is denoted as ⋆ in the figure) started appearing from 200 °C onwards; its crystallinity enhanced (as deduced from both increase in the intensity and sharpness of the reflections) with a further increase in calcination temperature. These results are in accordance with the thermogravimetric results and it can be safely concluded that hydroxylated layered network prevails for MgAl (in situ PXRD showed the prevalence of the layered lattice upto 360 °C) and NiAl catalysts, while such a network was absent for the other bivalent systems. In other words, such hydroxylated network is essential for mediating eugenol isomerization. To our knowledge this is the first report, which shows the necessity of a layered hydroxyl network for a base-catalyzed organic transformation on as-synthesized hydrotalcites. Choudary et al. [32] have earlier made similar attributions on the importance of layered lattice for activity, however, for the oxidation of allylic and benzylic alcohols using molecular oxygen as oxidant over NiAl binary hydrotalcite. Based on the above results, Mg and Ni as bivalent metal cations were selected for further study.

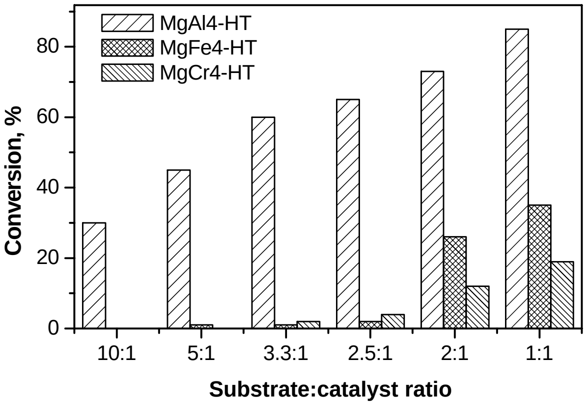


Fig. 5. Variation of substrate:catalyst mass ratio for isomerization of eugenol over MgM(III)-4HTs (conditions as given in Table 2).

3.2.4. *Influence of trivalent metal ion*

In an endeavor to study the influence of trivalent cation, a series of hydrotalcites of general formula MgM(III)-4HT, where M(III) = Al, Fe, Cr or V with Mg/M(III) atomic ratio of 4.0, were tested for isomerization of eugenol. Among the catalysts studied, MgAl-4HT offered maximum conversion of 73%, followed by Fe, Cr and V, which showed 26, 12 and 6% conversion, respectively. A first look at the conversion trend would suggest a correlation with the crystallinity of the compounds, wherein PXRD showed a maximum crystallinity for Al followed by Fe and Cr (HT-like phase was not observed for vanadium). In addition, variation of substrate:catalyst ratio, presented in Fig. 5, substantiated the results, wherein a continuous increase in the conversion was noted with a decrease in this ratio for all the three catalysts, though all exhibited a similar trend irrespective of this ratio. These results were further augmented by TG results (shown in Fig. 6), which showed a maximum thermal stability for Al-containing hydrotalcite followed by Fe- and Cr-containing materials. Subsequently, further studies were done using Al as trivalent metal ion.

In an attempt to alter the acid–base properties with an anticipation of some impact on the catalytic activity, a partial substitution of Al in MgAl-4HT by La, Zr and Ga was done. In all cases, a drop in the conversion was noted compared to that of MgAl-4HT (45% conversion at a substrate:catalyst ratio of 5:1 at 200 °C for 6 h), wherein 1% conversion was noted when Al was equivalently substituted by Zr, 4% by La and 25% when substituted by Ga under similar reaction conditions. In addition, the conversion was higher when the concentration of other trivalent and tetravalent atoms was lower. For example, a 10 at.% substitution of Al by Zr in MgAlZr ternary hydrotalcite yielded a conversion of 28% while 20 at.% of Ga substitution resulted in 30% of conversion of eugenol. These results suggest that substitution of Al by other trivalent or tetravalent ions either covers/destroys the active sites offered by Al or alters the basic strength of the sites, thereby decreasing the conversion.

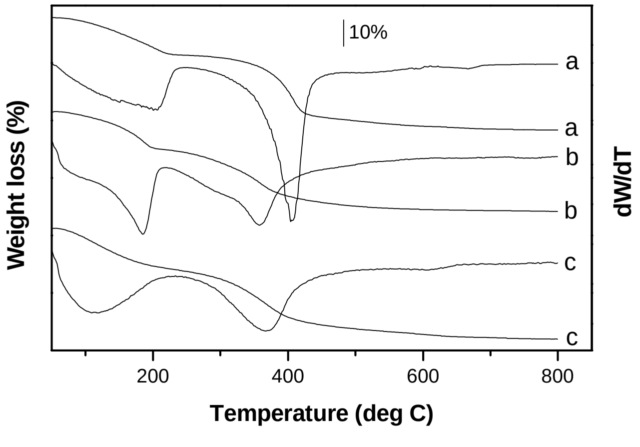
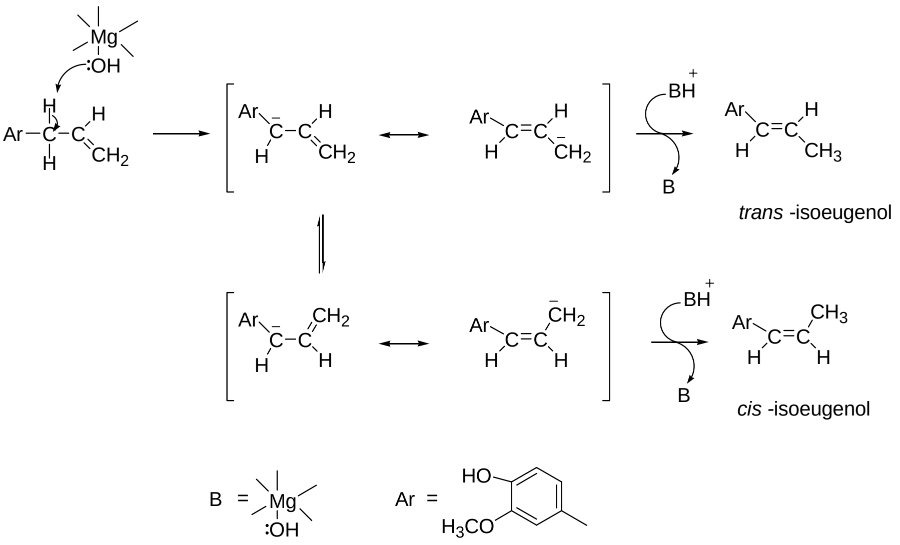


Fig. 6. TG–DTG patterns of: (a) MgAl-4HT; (b) MgFe-4HT; (c) MgCr-4HT.

3.2.5. *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 eugenol isomerization. The temperatures were chosen based on thermoanalytical results. In general, reports are largely available on the utilization of calcined hydrotalcites as solid catalysts for base-catalyzed organic reactions such as condensation, dehydrogenation and isomerization [18,20]. Our studies indicated a drop in the conversion of eugenol for the calcined samples compared to as-synthesized samples. However, the decrease was not remarkable upto 400 °C (40% conversion using substrate:catalyst ratio of 2:1) while a sharp fall was noted with a further increase in temperature (less than 3% conversion at both 600 and 800 °C). The probable reason for such a drastic drop in the conversion may be structural change, wherein complete destruction of layered structure occurs at higher temperatures (>500 °C), forming mixed metal oxide. Our recent study on probing the acid–base characteristics of calcined MgAl-HT through low temperature CO adsorption by FT-IR showed the presence of Lewis base sites at those temperatures [33]. In other words, one can say that eugenol isomerization is not effective on Lewis basic sites and requires Bronsted basic sites (hydroxylated layered network), which abstract protons of methylene carbon to assist in isomerization. A probable mechanistic pathway for isomerization of eugenol over MgAl binary hydrotalcite is depicted in Scheme 2.

Additional experiments were carried out to see the influence of “ex situ” heating and reaction atmosphere. To find out the influence of reaction atmosphere, we carried out eugenol isomerization over MgAl-4HT under nitrogen. The conversion decreased (44% at 200 °C using substrate:catalyst mass ratio of 2:1) under inert conditions, suggesting the non-influence of atmosphere on the basic sites of these materials in catalyzing the reaction. This is advantageous in view of the general hurdle posed by basic catalysts prone to CO_2 and/or H_2O poisoning, forcing one to operate under inert conditions. Further, when the same catalyst was externally calcined at 200 °C for 5 h in air



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

and tested for the reaction, the conversion of eugenol (39% conversion with *cis*:*trans* ratio of 10:90) was less than for the fresh catalyst, suggesting the superior nature of basic sites generated in situ under reaction conditions. Furthermore, when MgAl-4HT was calcined in situ under nitrogen at 200 °C for 5 h and subjected to reaction mixture without exposing the catalyst to air, the conversion improved (50% with *cis*:*trans* ratio of 23:77); however, the results also showed some undesired higher organic products (not detected by GC; quantification by external standard). In toto, reaction under simple conditions, generating the active catalyst in situ, resulted in maximum conversion with good yield of isoeugenol, without forming undesired products.

3.2.6. *Influence of co-bivalent metal ions*

The observation of high conversion of eugenol over Mg and Ni containing binary hydrotalcites prompted us to look for possibilities of synergism. Thus, ternary hydrotalcite systems having both Mg and Ni as bivalent metal ions were synthesized with varying Mg/Ni atomic ratios and studied for isomerization of eugenol (Table 5). For comparison, activities of MgAl-4HT and NiAl-4HT are also included in Table 5. Conversion as high as 90% was noted for MgNiAl15-HT with a *cis*:*trans* ratio of around 16:84 using a substrate:catalyst mass ratio of 2:1. To our knowledge, this is the highest conversion reported in the literature so far on any heterogeneous catalyst. Such a high yield of isoeugenol under environmentally benign conditions suggests the possibility of exploring these catalysts on a larger scale. However, for other catalysts studied in this series, mixed results were noted when compared to binary systems. In an endeavor to find the activity variation with Mg/Ni atomic ratio, the reaction was carried out using a substrate:catalyst mass ratio of 5:1. Similar results were obtained at this ratio also, wherein MgNiAl15-HT showed maximum conversion (66% conversion with 8:92 *cis*:*trans* ratio while MgAl-4HT showed 45% conversion with 22:78 *cis*:*trans* ratio). Among the catalysts studied, however, no regular variation was noted with Mg/Ni composition. These results suggest that co-presence of both Mg and Ni together in a HT-like lattice will promote a co-operative phenomenon for such systems, exhibiting altered reactivity. In our recent publication, we showed the operation of such synergism on transition metals containing hydrotalcites for hydroxylation of phenol [34].

In addition, to see the influence of other co-bivalent metal ions on MgAl system which were not showing significant conversion as binary systems, such as Zn, Co and Cu, we synthesized ternary systems such as MgM(II)Al-HT, where M(II) = Zn, Co and Cu with Mg/M(II) atomic ratio of 5.0 and 0.2. These compositions were selected to see their influence at both low and high concentrations on the isomerization activity. At smaller concentrations of co-bivalent metal ion, a sharp drop in the activity (MgZnAl51-HT-13; MgCoAl51-HT-3%; MgCuAl51-HT-nil) was noted, while at higher concentrations, no activity was noted irrespective of co-bivalent metal ions. A similar observation was noted for NiAl binary hydrotalcite also, wherein a small addition of zinc to NiZnAl51-HT ternary system dropped the

Table 5
Isomerizaton of eugenol over MgNiAl-HTs[a]

Catalyst	Conversion (%)	Product distribution (%)		Surface area (m^2/g)
		Cis-isomer	*Trans*-isomer	
MgNiAl-51HT	59	20	80	119
MgNiAl-31HT	65	17	83	90
MgNiAl-11HT	53	21	79	67
MgNiAl-13HT	85	15	85	83
MgNiAl-15HT	94	16	84	144
MgAl-4HT	73	16	84	83
NiAl-4HT	75	15	85	125

[a] Reaction parameters as given in Table 2.

activity from 75% for binary system to around 17% conversion of eugenol. Such a sharp decrease in the activity even upon small incorporation of inactive metal ions in MgAl or NiAl layered lattice would suggest a strong negative influence of these metal ions in altering the basic characteristic of the hydroxyl groups, and in turn a similar influence on the activity.

3.2.7. *Influence of alkali metal ion and ruthenium loading*

Many base-catalyzed organic transformations have been promoted by impregnating with alkali metal ions, especially on zeolites 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 or ruthenium over MgAl-4HT through impregnation. The results evidenced that incorporation of ruthenium as well as of alkali metal ions improved the conversion compared to as-synthesized hydrotalcite. In addition, a trend was observed wherein the conversion increased with an increase in ruthenium content. A conversion of as high as 71% with a *cis*:*trans* ratio of 25:75 was noted for 2.5% Ru-incorporated hydrotalcite (ICP analysis showed a loading of 1.8% of Ru) against 45% conversion (*cis*:*trans* ratio of 22:78) for as-synthesized MgAl-4HT with a substrate:catalyst ratio of 5:1 (∼18:1 substrate:catalyst mole ratio) under identical reaction conditions. To our knowledge, this is the highest conversion reported at such low catalyst concentration for this reaction. Similarly, conversion improved with alkali metal ion doping, except for lithium, wherein Cs showed maximum activity (57% conversion with *cis*:*trans* ratio of 18:82); the trend was in accordance with the basicity of alkali metal ions. Further, in an endeavor to compare the activity with conventional bases, we carried out eugenol isomerization over KOH and $KOBu^t$. On KOH, with a substrate:catalyst ratio of 1:10, a conversion of 9% was noted, while a further decrease in substrate:catalyst ratio to 1:20, showed a conversion of 13% at 200 °C. On $KOBu^t$, a conversion of around 5% was noted using a substrate:catalyst ratio of 1:3 at 200 °C, using DMF as solvent. Further, mass balance calculations for these catalysts showed a poor quantification, suggesting that there may be some undesired reactions leading to higher organics, undetected by GC.

4. Conclusions

Isomerizaton of eugenol to isoeugenol was carried out over different series of hydrotalcites of general formula M(II)M(III)-CO_3-HTs, where M(II) = Mg, Ni, Co, Cu and Zn and M(III) = Al, Fe, Cr, V and La, with different metal ion combinations and atomic ratios. Among various binary hydrotalcites studied with Al as trivalent cation, Mg and Ni showed maximum activity, while all the other bivalent metal ions showed poor activity. Thermal stability and structural integrity of layered lattice are thought to be indispensable for this reaction. Trivalent metal ion variation revealed maximum activity for Al, followed by Fe and Cr, and a direct correlation was noted between 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. Synergism was noted when highly active Mg and Ni were present together in the layered lattice as ternary hydrotalcite. MgNiAl-15HT showed 94% conversion of eugenol with a *cis*:*trans* ratio of around 16:84 using substrate:catalyst mass ratio of 2:1 at 200 °C, which is the highest conversion ever reported on a solid base catalyst for this transformation. Alkali metal ions and ruthenium impregnation showed improved conversion. Comparison with conventional bases indicated the superiority of hydrotalcite-derived catalysts at higher substrate:catalyst ratios, in addition to their environmental advantages. Efforts to test these catalysts on larger scale are in progress.

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