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Isomerization of eugenol and alkenyl aromatics of perfumery interest over Ni-containing layered double hydroxides as solid base catalysts

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ABSTRACT

Isomerization of eugenol was carried out over M(II)Al binary hydrotalcites where M(II) = Mg, Ni, Cu, Li or Co with M(II)/Al atomic ratio of 3.0. All samples were synthesized by coprecipitation under low supersaturation and characterized by powder X-ray diffraction (PXRD), FT-IR, thermogravimetry and BET N_2 adsorption measurements. All samples showed PXRD profiles similar to HT-like phase except for copper, which showed additional reflections of impurity phases. Among the catalysts studied, NiAl3-HT offered maximum conversion of eugenol to isoeugenol of around 77% at 200 °C in 6 h using DMF as solvent. CuNiAl ternary hydrotalcites with (Cu + Ni)/Al atomic ratio of 3.0 with varying Cu:Ni atomic ratios were synthesized and tested for isomerization of eugenol. Addition of copper in NiAl HT-like lattice significantly reduced the isomerization activity wherein 25% substitution of Cu^{2+} for Ni^{2+} completely annihilated the activity. To study, the influence of synthesis methodology, NiAl3-HT was also synthesized through urea and hexamine hydrolysis wherein sample prepared by former method offered maximum crystallinity among all samples synthesized. However, no isomerization of eugenol was seen for these samples except for the sample obtained through coprecipitation. The observed activity trends could reasonably be correlated with the basicity of the catalysts obtained using phenol adsorption measurements. The catalyst could be reused for two times without much decrease in the activity while further reuse resulted in decrease in the activity. The versatility of the catalyst was checked through isomerization of various alkenyl aromatics wherein at 160 °C, allyl benzene showed maximum conversion to β-methyl styrene and eugenol showed minimum conversion.

1. Introduction

The isomerization of alkenyl aromatics (Scheme 1) such as eugenol, estragole, dimethoxy allylbenzene and allylbenzene is an important *trans*formation wherein the corresponding *iso*-compounds bestow applications in pharmaceuticals and industries concerned with fragrance field [1,2]. Conventionally these reactions are catalyzed by alkalis such as KOH in alcoholic solutions (most often in higher alcohols) at high temperatures. These bases are generally used in stoichiometric or superstoichiometric quantities to that of the compound being isomerized, resulting in large quantities of caustic waste streams and posing handling problems. Previous attempts on isomerization of eugenol were done under homogeneous conditions using alcoholic alkali solution [3] either conventional or microwave irradiation at high base concentrations [4] usually at their refluxing temperatures. It is also reported that when equivalent or sub-stoichiometric quantities of alkali are used, poor yields of isoeugenol is obtained [3] while high boiling alcohols such as glycerol or glycol offered better conversion of eugenol in shorter time [4,5]. The predictability of replacing liquid catalysts with solid base catalysts for these *trans*formations is quite obvious for cleaner environment and easier separation [6–8] in addition to energy implications. There are reported works on isomerization of eugenol and safrole over palladium on alumina catalyst in the liquid phase [9] and over KF on neutral alumina in ethylene glycol [3,10]. The isomerization always gives a mixture of both *cis* and *trans* isomers while the later is thermodynamically more stable than the former. For all practical purposes, since *cis* and *trans* isomer possess similar behavior, there is no necessity in separating them for targeted applications.

Among various solid base catalysts studied in literature, hydrotalcite-like (HT-like) compounds are receiving an increasing attention for diversified base-catalyzed reactions [11–13]. To briefly introduce, they are layered materials with $Mg(OH)_2$

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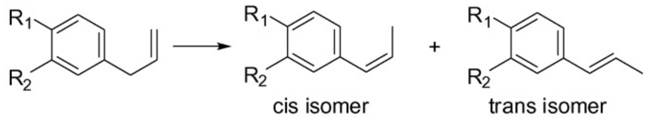

$R_1 = H$; $R_2 = H$ – Allyl benzene

$R_1 = OH$; $R_2 = OCH_3$ – Eugenol

$R_1 = OCH_3$; $R_2 = H$ – Estragole

$R_1 = OCH_3$; $R_2 = OCH_3$ - Dimethoxyallylbenzene

Scheme 1. Isomerization of alkenyl aromatics.

structure wherein partial substitution of Mg^{2+} by Al^{3+} occurs and the excess positive charge density is compensated by anions which occupy between the sheets along with water molecules [14]. Earlier, we have presented our first results on isomerization of eugenol and safrole over MgAl binary hydrotalcites as solid base catalysts [15]. It is also known in the chemistry of hydrotalcites that, changing the nature of the cations in the layers, M^{2+}/M^{3+} ratio, nature of the compensating anions or activation/synthesis methodology can modify the acid–base and redox properties of these materials and in turn on their catalytic behavior [16,17]. The present work divulge investigation on various HT-like materials, in particular, those containing nickel for isomerization of different alkenyl aromatics, in particular, for eugenol.

2. Experimental

2.1. Sample preparation

All samples were prepared by the low supersaturation technique unless otherwise mentioned. A solution (A) containing the desired amount of metal (Mg, Li, Ni, Co, Cu, Al) nitrates were mixed with a solution (B) containing precipitating agents (i.e., NaOH and Na_2CO_3) slowly (1 ml/min) and simultaneously in a Schott autotitrator assembly (Titroline, Schott, Germany) while maintaining the pH at 9.5 ± 0.1 under stirring at room temperature. The addition took 90 min and the final pH was adjusted to 10. The samples were aged in the mother liquor at 65 °C for 18 h, filtered off, washed (until total absence of nitrates and Na in the washing liquids) and dried at 100–110 °C for 12 h [18]. The samples are represented here 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

Powder X-ray diffraction (PXRD), carried out on a Philips X'Pert MPD system using Cu Kα radiation. The operating voltage and current were 40 kV and 30 mA, respectively. The step size was 0.04° with a step time of 2 s. Identification of the crystalline phases was made by comparison with the JCPDS files [19].

FT-IR spectra were recorded in a PerkinElmer 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.

Themogravimetric (TG) analysis was carried out in a Mettler TGA/SDTA 851^e and the data were processed using Star^e software, in flowing nitrogen (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 80 °C for 4 h prior to measurements and the data were analyzed using published software [20].

2.3. Isomerization of alkenyl aromatics

Isomerization of alkenyl aromatics was conducted in a batch reactor (50 ml), wherein the substrate, solvent and catalyst were charged at once and subjected to a preheated oil bath at reaction temperature [15]. The products were withdrawn using a syringe at definite time intervals and analyzed by gas chromatography (Shimadzu-14B, OV-17) using FID. Identification of the products was also further verified using GC–MS (Shimadzu QP 2010).

2.4. Phenol adsorption

To probe the basic sites of the catalysts, we carried out phenol adsorption measurements as published earlier [21]. Standard solutions of phenol in cyclohexane were prepared at 25 °C (0.01, 0.02, 0.04, 0.06 and 0.08 mmol). 25 ml of the each standard solution was taken in separate conical flasks to which 50 mg of catalyst was added and each mixture was kept in a shaker for three hours. After equilibrium was reached, catalysts were removed by centrifuging. Care must be taken that adsorption measurements should be done at 25 °C as the temperature co-efficient of expansion was higher for this phenol:cyclohexane mixture. The amount of phenol adsorbed by the catalysts was measured by UV–vis spectroscopy (λ_{max} = 271 nm).

3. Results and discussion

3.1. Isomerization of eugenol over M(II)Al binary hydrotalcites

Isomerization of eugenol over M(II)Al binary hydrotalcites where M(II) = Mg, Ni, Co, Cu or Li with M(II)/Al atomic ratio of 3.0 was carried out whose data are summarized in Table 1. Powder X-ray diffraction of all samples, except, CuAl3-HT, showed diffraction pattern (given in Supplementary Information, Fig. 1S) similar to that of hydrotalcite (JCPDS: 41-1428), wherein maximum crystallinity was shown by NiAl3-HT and MgAl3-HT. The diffraction pattern of CuAl3-HT was a mixed phase containing both HT-like phase along with malachite and/or gerhardite phase as observed earlier by us [22]. It is known that Cu^{2+} could not be crystallized in HT-like lattice due to Jahn-Teller distortion [23]. Among the samples screened, NiAl3-HT showed maximum conversion of 77% with 16:84 *cis*:*trans* ratio at 200 °C using DMF as solvent at substrate:catalyst mass ratio of 2:1. The *trans* isomer is formed in preference due to its better thermodynamic stability. All the other metal ions, except MgAl3-HT (24%), showed very low conversion (<10%) under similar conditions suggesting

Table 1
Influence of bivalent metal ions in M(II)Al3-HT for isomerization of eugenol

Catalyst[a]	Conversion (%)	Product distribution (%)	
		cis	*trans*
MgAl3-HT	24	26	74
LiAl3-HT	8	12	88
CoAl3-HT	3	49	51
NiAl3-HT	77	16	84
CuAl3-HT	2	0	100
$Ni(OH)_2$	0	0	0
Synthetic HT[b]	0	0	0

[a] Substrate: eugenol (500 mg); solvent: DMF (20 ml); catalyst weight (250 mg); reaction temp/time: 200 °C/6 h.

[b] Of M/s Aldrich Product Number: 652288.

the appropriate strength of basic sites are present in NiAl system. It has been mentioned earlier on the unique acid–base behavior of Ni-containing hydrotalcites for base-catalyzed reactions [24–26].

The basic behavior of NiAl-LDH has been explained earlier by Choudary et al. [24] for selective oxidation of alcohols. Recently, Jana et al. [25] discussed the basic character of Ni-containing HTs, and explained that the basicity increases with an increase in nickel content. To understand the basicity of these catalysts, phenol adsorption measurements, a methodology to unravel surface basic character of the solid catalysts, were carried out at 25 °C whose isotherms of some of the samples are summarized in Fig. 1. Among the bivalent metal ions, those which has Mg or Ni in the sheets showed high phenol adsorption suggesting stronger basic character of these catalysts, as recently reported by us [27]. Reasonable correlation of the isomerization activity for Mg and Ni-containing hydrotalcites with the phenol adsorption values suggest the necessity of Bronsted basicity in driving the reaction. To check the necessity of HT-like lattice, $Ni(OH)_2$ was synthesized (without trivalent metal ion) by similar coprecipitation technique and studied for isomerization. Surprisingly, no conversion was noted for simple metal hydroxide indicating the importance of HT-like lattice. The low phenol adsorption capacity of $Ni(OH)_2$ (Fig. 1) suggest a poor basic character of this catalyst, in turn, may be responsible for the inactivity. This result infers that incorporation of Al^{3+} in $Ni(OH)_2$ thereby creating HT-like lattice influences both nature and access of the structural hydroxyl groups, thereby offering good conversion. It is generally known that $Ni(OH)_2$ is acidic in nature and hence finds major application in the rechargeable batteries [28–30], while nickel in HT-like structure possesses the basic character which is essential for driving this reaction. In an interest to find the activity of commercially available hydrotalcite (M/s Aldrich: MgAl-HT with Mg/Al atomic ratio of 3 with BET surface area of around 9 m^2/g) isomerization of eugenol was carried out for this sample. Here again, no isomerization activity was found despite its very high crystallinity. A closer observation of the reaction mixture indicated that the catalyst floated over the reaction mixture. Upon vigorous stirring, catalyst particles stuck on the walls of the reactor and only about less than 5% of the catalyst settled suggesting poor contact with reaction mixture (probably due to low bulk density of the sample as it had very small particles; more than 80% of the particles are with less than 1 μm). However, our catalysts settled and heterogeneously well mixed with the reaction mixture.

3.2. Isomerization of eugenol over NiCuAl ternary hydrotalcites

Having known the superior performance of Ni-based system for isomerization of eugenol, an interest emerged to see the influence of addition of Cu, which exhibits very low activity for this *trans*formation, in the binary NiAl lattice (resulting in a ternary NiCuAl HT-like network) in an anticipation of observing cooperative phenomenon. Accordingly, catalysts with general formula NiCuAlyz-HT having (Ni + Cu)/Al atomic ratio of 3.0 with carbonate as interlayer anion with varying Ni/Cu atomic compositions were synthesized by coprecipitation under low supersaturation. PXRD of these samples showed pattern similar to HT-like phase wherein a progressive shift in the basal reflections ((0 0 3) and (0 0 6) planes) to higher angles and 'ab' plane reflection namely (1 1 0) (appearing around $2\theta = 60^\circ$) to lower angles (as evidenced from the lattice parameters values '*a*' and '*c*' summarized in Table 2) were noted upon increase in the concentration of copper. Table 2 also summarizes textural parameters of the samples measured through nitrogen adsorption measurements whose adsorption–desorption profiles showed Type II isotherm (according to IUPAC classification) with hysterisis (at higher P/P_0) attributed to capillary condensation with nearly unimodal pore size distribution centering in mesopore regime. It can be seen from this table that no significant variation in the specific surface area (140 ± 20 m^2/g), average pore diameter (11–12 nm) and pore volume (0.45 ± 0.05 cm^3/g) of these samples with the variation in copper concentration suggesting no significant change in particle characteristics.

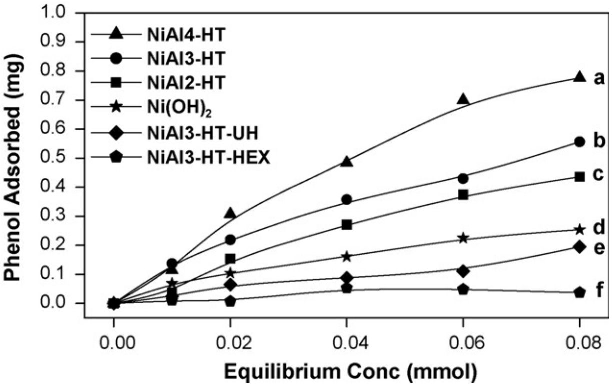

Fig. 1. Phenol adsorption studies of some of the samples synthesized.

Table 2
Crystallographic and textural parameters of NiCuAl ternary hydrotalcites

Catalyst	Lattice parameters		Surface area[a]	Pore volume[b]
	a (Å)	*c* (Å)		
NiAl3-HT	3.041	23.361	145	0.42
NiCuAl9802-HT	3.043	23.241	142	0.41
NiCuAl9505-HT	3.043	23.219	142	0.43
NiCuAl9010-HT	3.046	23.211	162	0.50
NiCuAl7525-HT	3.049	22.851	162	0.45
NiCuAl5050-HT	3.059	22.827	128	0.39

[a] Specific surface area in m^2/g.
[b] Pore volume in cm^3/g.

Table 3 summarizes the isomerization activity of NiCuAl ternary HTs towards eugenol. Among the catalysts studied, NiAl3-HT exhibited highest conversion of 77% with *cis*:*trans* ratio 16:84 at 200 °C with a substrate:catalyst mass ratio of 2:1. In all the cases *trans* isomer predominates with around 85%, due to its better thermodynamic stability. Addition of copper in NiAl binary lattice strongly decreased the conversion of eugenol. For example, 25% substitution of Cu^{2+} in binary NiAl lattice (NiCuAl7525-HT) completely annihilated the activity for this reaction. Specific surface areas of these samples also had very less influence in the isomerization activity for eugenol. On the contrary, among the samples studied, the sample with maximum surface area namely, NiCuAl7525-HT (162 m^2/g), is inactive for enabling this isomerization. To understand further, a well ground homogeneous physical mixture of NiAl3-HT and CuAl3-HT was made in the Ni:Cu mole ratio of 3:1 (similar to the sample NiCuAl7525-HT) and tested for isomerization of eugenol. A conversion of around 17% was noted for this physical mixture against no conversion for NiCuAl7525-HT suggest Cu^{2+} when present in the lattice along with Ni^{2+} modify acid–base and/or electronic behavior thereby not catalyzing the reaction. These results suggest, although materials employed in this study possess similar textural characteristics with nearly similar crystallinity, a strong variation in the activity upon Cu^{2+} substitution could be either due to significant variation in the basicity or profound electronic effects [31]. A detailed study on the influence of copper ions in NiAl binary lattice on the isomerization activity is underway.

Table 3
Isomerization of eugenol over NiCuAl ternary hydrotalcites

Catalyst[a]	Conversion (%)	Product distribution (%)	
		cis	*trans*
NiAl3-HT	77	16	84
NiCuAl9802-HT	42	27	73
NiCuAl9505-HT	47	21	79
NiCuAl9010-HT	24	34	66
NiCuAl7525-HT	0	0	0
NiCuAl5050-HT	5	0	100
CuAl3-HT	2	0	100

[a] Substrate: eugenol (500 mg); solvent: DMF (20 ml); catalyst weight: 250 mg; reaction temp/time: 200 °C/6 h.

Table 4
Influence of synthesis methodologies on the isomerization of eugenol

Catalyst[a]	Conversion (%)	Product distribution (%)		Surface area[c]
		cis	*trans*	
NiAl3-HT[b]	77	16	84	145
NiAl3-HT-UH	1.5	0	100	38
NiAl3-HT-HEX	0.13	0	100	2
NiAl3-HT-HEX HYD	0.32	0	100	ND[d]
NiAl2-HT[b]	54	25	75	152
NiAl4-HT[b]	82	19	81	127

[a] Substrate: eugenol (500 mg); solvent: DMF (20 ml); catalyst weight: 250 mg; reaction temp/time: 200 °C/6 h.
[b] Sample synthesized by coprecipitation.
[c] Specific surface area in m^2/g.
[d] ND: not determined.

3.3. Influence of synthesis methodology on the isomerization of eugenol

In an endeavor to further improve the conversion of eugenol to *iso*-eugenol, the most active catalyst NiAl3-HT was synthesized using urea (UH) and hexamine hydrolysis (HEX). It is also known that synthesis methodology play an important role on the final properties and in turn on the catalytic activity for these materials [32,33]. Some of the samples were also subjected to hydrothermal (HYD) treatment to improve the crystallinity. In brief, the hydrolysis of metal nitrates was carried out using urea or hexamine as precipitating agents over a long time (~24–36 h) at 80–100 °C. Such slow and controlled hydrolysis is known to assist homogenous precipitation of metal ions thereby resulting in good crystalline material. PXRD profiles of some of the samples are given in Fig. 2. For sake of comparison, the sample synthesized through conventional coprecipitation is also given in Fig. 2. It is quite clear from the figure that all samples exhibited single phase HT-like structure without co-crystallization of discrete impurity phases. The peak positions of all reflections were nearly similar for the samples synthesized by urea hydrolysis (NiAl3-HT-UH) and coprecipitation while d_{003} and d_{006} reflections were shifted to lower angles for the sample synthesized through hexamine hydrolysis. The peak position of d_{003} reflection (d = 8.8 Å for NiAl3-HT-HEX) would suggest the intercalation of nitrate while for the samples obtained through urea hydrolysis and coprecipitation, the charge compensating anion is carbonate. This is further evidenced through FT-IR spectroscopy from the band positions, in particular, asymmetric stretching vibrations of nitrate and carbonate (Supplementary Information, Fig. 2S). All samples (except NiAl3-HT-HEX) showed prominent bands around 3475, 1642 and 1373 cm^{-1} correspondingly attributed to ν_{OH} stretching, δ_{H_2O} and ν_3 asymmetric stretching of carbonate vibrations characteristic of HT-like materials. However, for NiAl3-HT-HEX, a prominent band at approximately 1382 cm^{-1} along with weak bands around 1440 and 1048 cm^{-1} is discerned confirms the presence of nitrate anions [34,35]. Hydrothermal treatment for the sample obtained through hexamine hydrolysis improved the crystallinity as evidenced through sharpening of all reflections and crystallite size measurements which showed nearly a four-fold increase (NiAl-HEX = 60 Å and NiAl-HEX-HYD = 240 Å). Table 4 summarizes eugenol isomerization activity for NiAl hydrotalcites synthesized through various synthesis methodologies. It is quite surprising to note that the sample obtained through coprecipitation alone yielded very high conversion of 77% while the samples synthesized through urea and hexamine hydrolysis resulted in very poor conversion of eugenol (<2%). This observed activity for these samples is strange (as the active metal ions are same and the compositions are similar) despite the fact that the best crystalline material is obtained for the sample prepared through urea hydrolysis. However, a reasonable correlation could be deduced between the activities of the catalyst with the amount of phenol adsorbed (Fig. 1) suggest the necessity of Bronsted basicity. Furthermore, textural parameters of the samples, given in Table 4, also corroborated the activity trend wherein maximum specific surface area was obtained for the sample prepared through coprecipitation while the other methods yielded very low specific surface areas.

3.4. Activation and recycle studies

It is in general known, that the calcined hydrotalcites are potential catalysts for various *trans*formations and well studied in

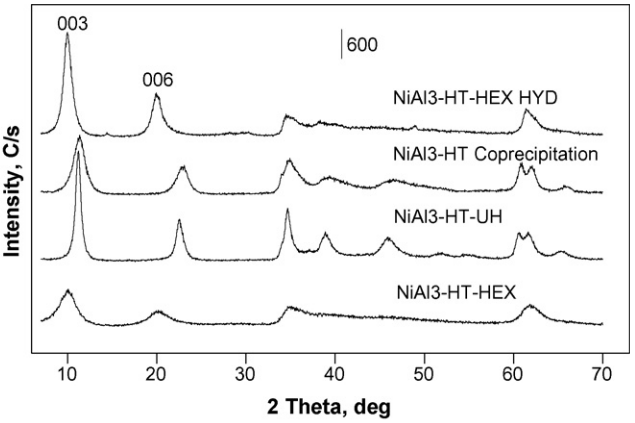

Fig. 2. PXRD profiles of NiAl3-HT synthesized by various preparation methodologies.

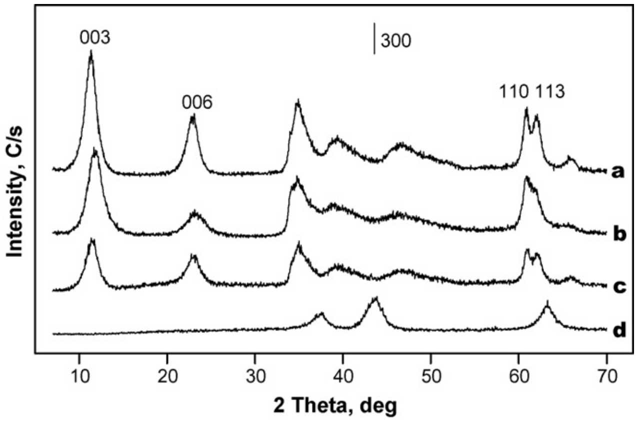

Fig. 3. PXRD of (a) NiAl3-HT, (b) NiAl3-HT heated at 200 °C for 6 h in air, (c) NiAl3-HT-used (after first catalytic cycle) and (d) NiAl3-CHT (calcined at 600 °C for 5 h in air).

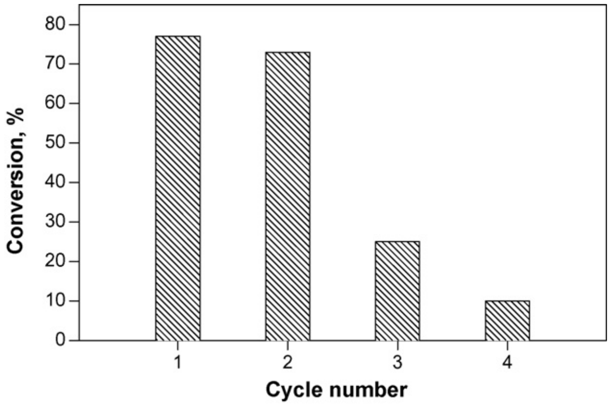

Fig. 4. Recycle behavior of NiAl3-HT for isomerization of eugenol.

literature [36–38]. In an anticipation of finding better catalyst, NiAl3-HT was calcined at 600 °C and tested for isomerization of eugenol. The diffuse PXRD pattern (Fig. 3) of this calcined material whose peak positions could be indexed for NiO phase (JCPDS: 4-835). No conversion of eugenol was noted for this calcined catalyst suggesting the necessity of hydroxylated layered lattice. In another experiment, the catalyst was suspended in solvent and heated at 200 °C for 1 h without adding eugenol. This experiment was done to infer whether in situ activation of eugenol over the catalyst while heating is critical for driving this reaction. A conversion of around 15% of eugenol was noted in 6 h for this reaction as against 77% conversion when all (catalyst, eugenol and solvent) were charged together and heated. To check the recyclability of these catalysts, the used catalyst was filtered, washed with deionized water, dried and checked for isomerization of eugenol, whose results are summarized in Fig. 4. No significant variation was noted for the second cycle, while a sharp decrease in the conversion was noted for the third (~25%) and fourth cycle (~10%). The PXRD profile of the used catalyst after first cycle is also included in Fig. 3, which showed HT-like phase although with a decrease in the crystallinity, suggesting the integrity of the catalyst. Further there is uniform broadening of the peaks upon heating suggests turbostratic disordering of the sheets [39]. We believe, such disordering may enhance the access of structural hydroxyl groups near the edges and thereby improve the activity. Very recently, de Jong and co-workers [40] have well articulated importance of accessibility of basic sites in HT-like materials for the base-catalyzed condensation reaction. Our earlier studies on the thermal stability of the NiAl-HT using variable temperature PXRD measurements suggested the retention of layered structure till 275 °C [41] which is also corroborated by TG measurements (Supplementary Information, Fig. 3S) wherein the second weight loss (dehydroxylation and decarbonation) occurred between 230 and 380 °C. The fall in the conversion for third and fourth cycle may probably due to the further decrease in the crystallinity of the catalyst.

Table 5
Isomerization of alkenyl aromatics over NiAl4-HT

Substrate[a]	Conversion (%)	Product distribution (%)	
		cis	*trans*
Allyl benzene	95	6	94
Estragole	86	15	85
Dimethoxy allyl benzene	30	12	88
Eugenol	18	13	87

[a] Solvent: DMF (20 ml); catalyst weight: 250 mg; substrate: 500 mg; reaction temp/time: 160 °C/6 h.

3.5. Isomerization of alkenyl aromatics over NiAl4-HT

Ni/Al compositional variation studies indicated (Table 4) that the activity increased with an increase in nickel concentration wherein highest conversion of eugenol was noted for NiAl4-HT (82%). Phenol adsorption studies (Fig. 1) showed an increase in the amount of phenol adsorbed with an increase in nickel concentration. A reasonable correlation between the isomerization activities (Table 4) with the amount of phenol adsorbed could be deduced. To check the versatility of these materials, similar compounds of alkenyl aromatics such as estragole, dimethoxy allylbenzene and allyl benzene along with eugenol were isomerized over this most active catalyst, NiAl4-HT. The reaction was conducted at a lower temperature, 160 °C, using DMF as solvent to discern the isomerization behavior of these substrates whose results are given in Table 5. Among the substrates screened, allyl benzene offered maximum conversion to β-methyl styrene (96%) while eugenol showed minimum conversion of around 18%. The variation in the activity of different alkenyl aromatics could be due to variation in the adsorption potential of the substrates on the surface of the catalyst. Addition of any functional group in benzene ring decreased the activity, wherein the decrease is larger when electron donating groups are attached. The retarding effect of electron donating substituent attached to phenyl ring on isomerization could be reasoned to a decrease in the acidity of the methylene proton ($-CH_2-$) of the allyl group whose abstraction by the basic site is the key step involved in the double bond migration. Analogous observation has been proposed by Yu et al. [42] for the isomerization of allyl aromatics using proazaphosphatrane. However, one cannot also rule out the possibility of variations in pK_a of these substrates for adsorption over these catalysts for enabling isomerization.

4. Conclusions

Among the various bivalent metal ions screened with M(II)/Al atomic ratio of 3.0, nickel offered maximum activity for the isomerization of eugenol, probably due to appropriate basicity of this catalyst. Addition of copper in the NiAl binary HT-like lattice significantly reduced the activity even at low concentration of copper. NiAl3-HT synthesized by coprecipitation offered maximum activity while very poor activity was noted for samples synthesized through urea and hexamine hydrolysis. Calcination of NiAl3-HT resulted in NiO which did not isomerize eugenol under our reaction conditions. Catalysts could be reused for two times while further reuse resulted in decrease in the yield of isoeugenol, probably due to the decrease in the crystallinity of the catalyst. Versatility of these materials is verified by isomerization of different substrates of perfumery interest, among which, allyl benzene isomerized in highest yield to β-methyl styrene at 160 °C. A reasonable correlation was deduced between the basicity of the catalysts obtained from phenol adsorption measurements with the activity of the catalysts. Further research is underway to unravel the influence of copper on the isomerization of eugenol over NiAl hydrotalcites.

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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.cattod.2008.03.023.

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