

Environmentally benign route for isomerization of safrole— hydrotalcite as solid base catalyst

D. Kishore, S. Kannan*

Silicates and Catalysis Discipline, CSMCRI, GB Marg, Bhavnagar 364002, India

Received 8 March 2003; received in revised form 27 August 2003; accepted 2 September 2003

Available online 21 September 2004

Abstract

Isomerization of safrole to isosafrole is an important reaction, involving double bond migration, catalyzed by bases. Hydrotalcites, solid bases, have been used for this double bond migration. Among the catalysts studied, MgAl hydrotalcite with Mg/Al atomic ratio 6.0 showed maximum conversion of around 98% with a *cis/trans* isosafrole ratio of 1/9 at 200 °C using DMSO as solvent. Solvent variation studies indicated that more polar solvents favored the reaction. Variation of trivalent metal ions showed a maximum activity for hydrotalcite containing Al, followed by Fe and Cr. Bronsted basic hydroxyl groups of hydrotalcite lattice are thought to be the active centers.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Isomerization; Safrole; Hydrotalcite; Crystallinity; Thermal stability

1. Introduction

Isomerization of safrole to the corresponding thermodynamically stable isosafrole is an important olefin isomerization reaction wherein the product finds application in fragrance and pharmaceutical industries [1,2]. Traditionally, this reaction is catalyzed by KOH in alcoholic solutions (most often in higher alcohols) at high temperatures. Alternatively, complexes of group VIII elements are used to catalyze the reaction [3]. Alkali metals supported on various aluminas, synthesized by impregnation at higher temperatures, were studied for isomerization of safrole [4]. A nearly 100% conversion was achieved around 1 h of reaction time at room temperature under nitrogen. However, this catalyst has inherent disadvantages during synthesis such as hazardous handling and environmental unfriendliness. Expensive metal complexes such as $(PPh_3)RhCl_2$ were used as catalysts for this reaction [5]. Cp_2TiCl_2 when used as catalyst [6] for this transformation under Grignard conditions ($BrCH_2CH_2Br/Mg/THF$) resulted in 80% conversion in 2 h

under nitrogen at room temperature. Qian et al. [7] have used the same catalyst, in presence of Mg alone and reported a higher conversion (92% with *cis/trans* ratio of 5/95) and proposed a highly unstable Cp_2Ti species (formed upon reduction of Cp_2TiCl_2 by Mg) as the active catalyst for the isomerization reaction. Radhakrishna et al. [8] have carried out isomerization of safrole on KF on neutral alumina in dry ethylene glycol and obtained around 76% yield at 150 °C. Conversion improved when they used ‘dry media’ without using any solvent [9]. However, in these cases, the amount of base employed was 10–20 times (w/w ratio) that of the substrate. Thach et al. [10] have obtained quantitative yields when they used KOH or KOtBu (1.2 mol equivalents) as catalyst in presence of a phase transfer agent, Aliquat 336. Recently, microwave assisted isomerization reactions were [11,12] done using both conventional bases, such as, KOH and KOtBu in alcohols as well as over KF/Al_2O_3 . An enhancement in the rate of the reaction using microwave compared to conventional refluxing attributed for local superheating, was observed. Replacement of conventional alkali based catalysts by solid base catalysts is one of the important tasks in view of effluent control and easy catalyst separation [13–15]. Hydrotalcite-like (HT-like)

* Corresponding author. Tel.: +91 278 2567760; fax: +91 278 2566970.
E-mail address: KanhEmad1@sancharnet.in (S. Kannan).

compounds are one of such promising heterogeneous solid base catalysts, which have been exploited for various base catalyzed transformations like aldol condensation [16], double bond isomerization of alkene [17] and dehydrogenation of 2-propanol [18]. They are layered materials with the general formula $[M(II)_{1-x}M(III)_x(OH)_2][A_{x/n}^{n-}] \cdot mH_2O$, where M(II) is the bivalent metal ion, M(III) the trivalent metal ion, A the interlayer anion and x can generally have the values between 0.2 and 0.35. Structurally, they possess brucite-like ($Mg(OH)_2$) layered network wherein a partial substitution of bivalent ion by trivalent ion, say Al^{3+} , occurs, and the resulting excess positive charge in the layers is compensated by anions located in the interlayers [19]. In this paper, we report the isomerization of safrole over MgM(III) hydroxalite-like compounds, where M(III) = Al, Fe and Cr. End members of the series namely $Mg(OH)_2$ and $Al(OH)_3$ were also synthesized and their activities reported.

2. Experimental

MgM(III) hydroxalites with different Mg/M(III) atomic ratios were synthesized by coprecipitation under low supersaturation [20]. A typical synthesis involves simultaneous addition of two solutions: Solution-A containing appropriate concentration of magnesium nitrate and trivalent nitrate solutions and Solution-B containing NaOH and Na_2CO_3 solutions as precipitants while maintaining the pH around 9–10 under vigorous stirring at room temperature. The precipitate was aged in the mother liquor at 65 °C for 18 h, filtered, washed thoroughly with distilled water (until total absence of nitrates and sodium in the filtrate) and dried at 110 °C for 12 h. The solids obtained here are referred as MgM(III)- x HT, where x stands for Mg/M(III) atomic ratio.

Elemental chemical analysis for Mg, Al, Fe and Cr was carried out by conventional wet chemical methods.

Powder X-ray diffraction (PXRD) patterns were recorded in a Philips X'pert MPD System, using Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) with a step size of 0.02 and step time of 1 s and processed using Philips X'pert Software. Identification of the crystalline phases was made by comparison with the JCPDS files [21].

Thermogravimetric (TG) analysis was carried out in Mettler TGA/SDTA 851^e and the data were processed using Star^e software, in flowing nitrogen or argon (flow rate 50 ml min⁻¹), at a heating rate of 10 °C/min.

Specific surface area and pore size analysis of these samples was 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 [22].

Isomerization of safrole was conducted in the batch mode in a two-neck glass reactor (50 ml) fitted with a condenser and a stopper, wherein the substrate, solvent and catalyst were all charged at once and raised to the reaction temperature at atmospheric pressure in air under stirring. Zero time was

taken after the attainment of desired reaction temperature. The progress of the reaction was monitored by withdrawing small amount of samples (0.05 cm³) using a syringe at definite time intervals and analyzed (using authentic samples) by gas chromatography (Shimadzu-14B, OV-17) using a flame ionization detector. Quantification of the products was done after due consideration of response factors of both reactant and products using isopropanol as external standard. Identification of the products was also further verified by 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 characterization of the samples

Table 1 summarizes the physicochemical properties of the samples synthesized. The elemental composition results showed a good correspondence between the solution Mg/M(III) ratio with the ratio obtained for solids suggesting completion of precipitation. However, deviations occurred at higher Mg/M(III) atomic ratio and for MgFe-6HT, probably due to preferential precipitation of one or the other cation as hydroxide [23] and incomplete precipitation, which is inherent in iron-containing systems [24], respectively.

Powder X-ray diffraction patterns of these samples are shown in Fig. 1. The samples showed sharp and symmetric reflections at lower diffraction angles and with broad asymmetric reflections at higher angles, characteristic of hydroxalite-like layered materials [25]. The peaks close to $2\theta = 11^\circ$, 24° and 35° , corresponding to spacings close to 7.6, 3.76 and 2.53 Å, respectively, are ascribed, assuming a 3R packing of the layers to diffraction by basal planes (003), (006) and (009). However, with an increase in Mg/Al ratio, the crystallinity of the HT-like phase decreased, as seen from broadening of the reflections (with poorer S/N ratio; the samples were recorded under identical conditions) and crystallization of discrete impurity phases (marked as * in the figure) when the Mg/Al atomic ratio was greater than 8.0. Analysis of the impurity peaks through peak-search-match procedure using JCPDS database revealed the formation of magnesium carbonate ($5MgO \cdot 4CO_2 \cdot 5H_2O$, JCPDS 01-0168). Variation of the lattice parameters, given in Table 1, showed an increase in both a and c with an increase in Mg/Al atomic ratio, attributed to higher octahedral ionic radius of Mg^{2+} (0.72 Å) than Al^{3+} (0.53 Å) and decreasing electrostatic interaction between layer and the interlayer. However, such an increase is up to a certain extent, while a further decrease in aluminum concentration did not significantly alter these values, possibly due to sustaining of the layered hydroxalite-like lattice. These results are substantiated by thermal analysis data, which are given below. Among the trivalent metal ions studied, Al offered maximum crystalline material followed by Fe and Cr [20,26]. MgCr-6HT showed a diffuse pattern of hydroxalite with broad reflections. However, the position of peak

Table 1
Physicochemical properties of the samples synthesized

Catalyst	Mg/Al atomic ratio		Lattice parameters		Specific surface area (m ² /g)	Pore volume (cm ³ /g)	TG parameters				
	Solution	Solid	<i>a</i> (Å)	<i>c</i> (Å)			<i>T</i> ₁	<i>T</i> ₂	<i>W</i> ₁	<i>W</i> ₂	Net
MgAl-2HT	2.0	2.0	3.04	22.85	102	0.51	243	416	16.42	21.04	37.46
MgAl-3HT	3.0	2.7	3.06	23.20	80	0.51	212	411	15.88	21.26	37.14
MgAl-4HT	4.0	3.5	3.07	24.41	83	0.47	205	403	13.71	23.67	37.38
MgAl-6HT	6.0	4.2	3.08	23.85	61	0.43	152	399	13.06	24.02	37.08
MgAl-8HT	8.0	5.8	3.09	24.12	49	0.37	140	404	12.35	26.59	38.94
MgAl-10HT	10.0	6.4	3.10	24.19	44	0.19	134	400	12.06	27.20	39.26
MgFe-6HT	6.0	2.7	3.03	22.90	75	0.43	178	355	13.52	19.97	33.49
MgCr-6HT	6.0	4.8	3.09	24.47	84	0.37	103	363	13.20	17.32	30.52

*T*₁ and *T*₂: transformation temperatures; *W*₁ and *W*₂: weight loss; net: total weight loss.

maximum is in correspondence with HT-like materials. The lattice parameters of the samples (Table 1), varied in accordance with the ionic radii of the metal ions [27]. The specific surface area and pore volume of the samples are also summarized in Table 1. A gradual decrease in the both specific surface area and pore volume was noted with an increase in Mg/Al atomic ratio, probably due to aggregation of particles. However, textural properties did not vary significantly with the variation in trivalent metal ion in the HT-like network.

Thermal analysis of all samples showed two well-defined weight losses pattern (Fig. 2). The first weight loss is due to

removal of water molecules present in the interlayer while the second weight loss is ascribed to the dehydroxylation of the hydroxyl network and decarbonation of interlayer carbonate anions resulting in collapse of the layered network. Evolved gas analysis (using quadrupole mass spectrometer) also confirmed (Fig. 2, inset) two stages of evolution of water and a sharp peak for CO₂ evolution. A well-defined twin peak, noted for H₂O evolution for the second weight loss for MgAl-6HT, is attributed to dehydroxylation at edges and sheets [28]. A small and continuous weight loss was observed at temperatures higher than 450 °C (<4%) probably due to evolution of strongly adsorbed CO₂. The transformation temperatures along with weight losses are also included in Table 1. A decrease in transformation temperature for complete destruction of layered network (*T*₂) occurs with

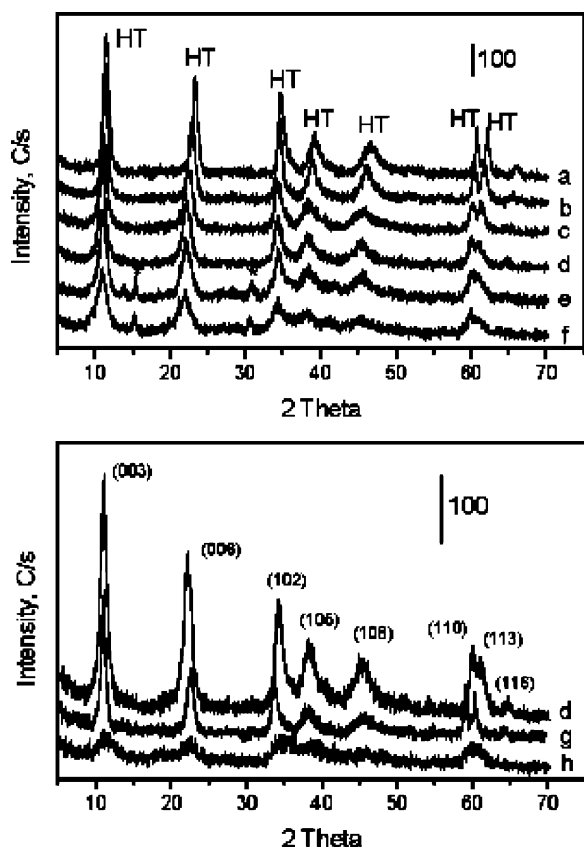


Fig. 1. Powder X-ray diffraction pattern of: (a) MgAl-2HT; (b) MgAl-3HT; (c) MgAl-4HT; (d) MgAl-6HT; (e) MgAl-8HT; (f) MgAl-10HT; (g) MgFe-6HT; (h) MgCr-6HT (HT: pattern in correspondence with synthetic hydroxylated JCPDS: 41-1428).

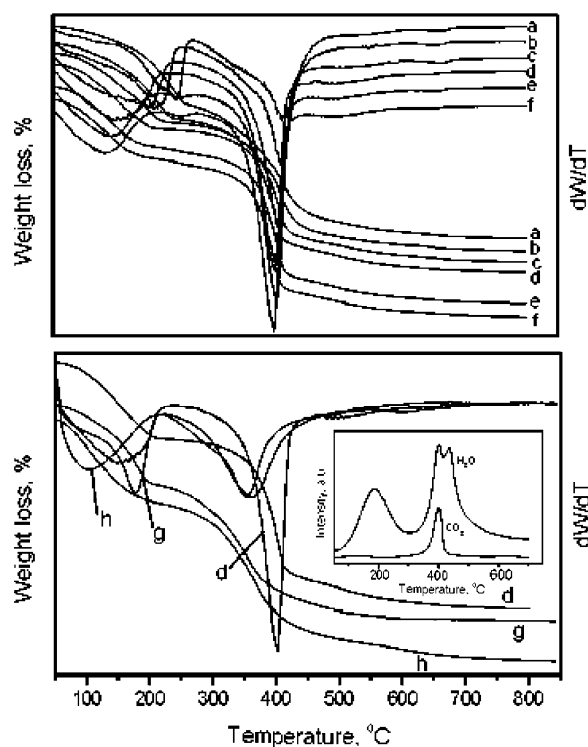


Fig. 2. TG-DTG curves of: (a) MgAl-2HT; (b) MgAl-3HT; (c) MgAl-4HT; (d) MgAl-6HT; (e) MgAl-8HT; (f) MgAl-10HT; (g) MgFe-6HT; (h) MgCr-6HT.

an increase in Mg/Al atomic composition (cf. PXRD results). This could be due to decrease in electrostatic interaction due to decrease in aluminum content. However, such a decrease was noted till Mg/Al atomic ratio 6.0 and did not significantly vary with a further increase in the ratio, suggesting similar extent of interaction. Among the trivalent cations studied, Al offered maximum thermal stability followed by Cr and Fe.

4. Catalytic studies

Table 2 summarizes the safrole isomerization activity of various MgAl hydrotalcites. End members, namely, Mg(OH)₂ and Al(OH)₃ are also included for comparison. Both showed poor conversions (Mg(OH)₂, 0.3 and Al(OH)₃, 0.1) while MgAl hydroxycarbonate crystallizing in HT-like network showed higher activity. The activity varied with the Mg/Al atomic ratio. Among the catalysts studied, MgAl-6HT showed maximum conversion of around 75% with a *cis:trans* ratio of around 15:85. Trans isomer was formed predominantly over all catalysts due to its better thermodynamic stability. Surprisingly, the activity of MgAl-2HT and MgAl-3HT were poor (2 and 1%, respectively) regardless they possess larger specific surface area and better thermal stability. In other words, despite the presence of stronger basic sites dispersed on a larger surface for these catalysts, could not result in significant conversion, probably suggests that the reaction prefer to occur on basic sites of an appropriate basicity. Attempt to study the basic strength requirements and basicity–activity correlation through physicochemical methods over these catalysts is underway. Conversion reached maximum with an increase in Mg/Al atomic ratio of up to 6.0 and decreased with a further increase in the ratio. From the results mentioned above, MgAl-6HT was selected for further study. Table 3 summarizes the activity of this catalyst for isomerization of safrole in different solvents. DMSO and toluene offered maximum activity of around 98% (with a *cis:trans* ratio of ~10:90). Solvent variation studies indi-

cated that the conversion increased with an increase in the polarity of the solvent (evidenced from the dielectric constants of the solvents, given in Table 3), except for toluene, for which the reasons are not clear. This is in accordance with the results reported by Tichit et al. [29] who observed a higher activity for the condensation of acetaldehyde with heptanal over calcined MgAl hydrotalcite for solvents with higher polarity. This may be due to improved desorption of product from the catalyst surface. Although both DMSO and toluene yielded good conversion, DMSO was selected for further study considering safety and loss on evaporation, as while using toluene bumping of the reaction mixture occurred violently (the external bath temperature was higher compared to the boiling point of the solvent). Fig. 3 shows the effect of substrate:catalyst mass ratio over MgAl-6HT using DMSO as solvent. Conversion increased with 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 conversion of around 95% in 1 h (98% in 6 h) was observed with a catalyst:substrate mass ratio of 1:2 (which is nearly 1:7.2 mole ratio) with a *cis:trans* ratio of around 17:83 (10:90). To our knowledge, this is the best result reported so far for this reaction over a solid base catalyst at such low catalyst concentration. Further, mass balance of the substrate was better than 95% suggesting selective isomerization without forming any additional or consecutive reaction products.

The variation of substrate:catalyst mass ratio over all the three catalysts for 1 h (MgAl-6HT, MgFe-6HT and MgCr-6HT) is also given in Fig. 3. A similar trend, which was mentioned earlier for MgAl-6HT, wherein conversion increased with a decrease in substrate:catalyst mass ratio, was observed for other trivalent cations also. Both the conversion and selectivities of isosafrole decreased in the following order: MgAl-6HT ~ MgFe-6HT > MgCr-6HT. This could possibly be due to lower thermal stability for Fe and Cr systems compared to Al (cf. TG results) and may also be ascribed as for differences in orderliness of the layered lattice. As expected conversion of safrole increased with an increase in reaction temperature (Fig. 4). The reaction was nearly complete (~95%) in 1 h. No significant variation in *cis:trans* isomer ratio of isosafrole was noted for all

Table 2
Isomerization of safrole over MgAl hydrotalcites with different Mg/Al atomic compositions^a

Catalyst	Conversion (%)	Product distribution (%)	
		<i>Cis</i>	<i>Trans</i>
MgAl-2HT	2	–	100
MgAl-3HT	1	–	100
MgAl-4HT	28	11	89
MgAl-6HT	75	15	85
MgAl-8HT	33	15	85
MgAl-10HT	54	15	85
Mg(OH) ₂	0.34	–	100
Al(OH) ₃	0.11	–	100
Blank	–	–	–

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

Table 3
Influence of solvent for isomerization of safrole over MgAl-6HT^a

Solvent	Conversion (%)	Product distribution (%)		Dielectric constant, ϵ
		<i>Cis</i>	<i>Trans</i>	
DMSO	98	10	90	47.2
Toluene	98	10	90	2.4
DMF	88	14	86	38.2
Acetonitrile	89	13	87	36.6
4-Methyl-2-pentanone	78	17	83	15.1
THF	60	17	83	7.5

^a Substrate: 0.5 g; catalyst: 250 mg; reaction temperature/time: 200 °C/6h; solvent volume: 10 ml.

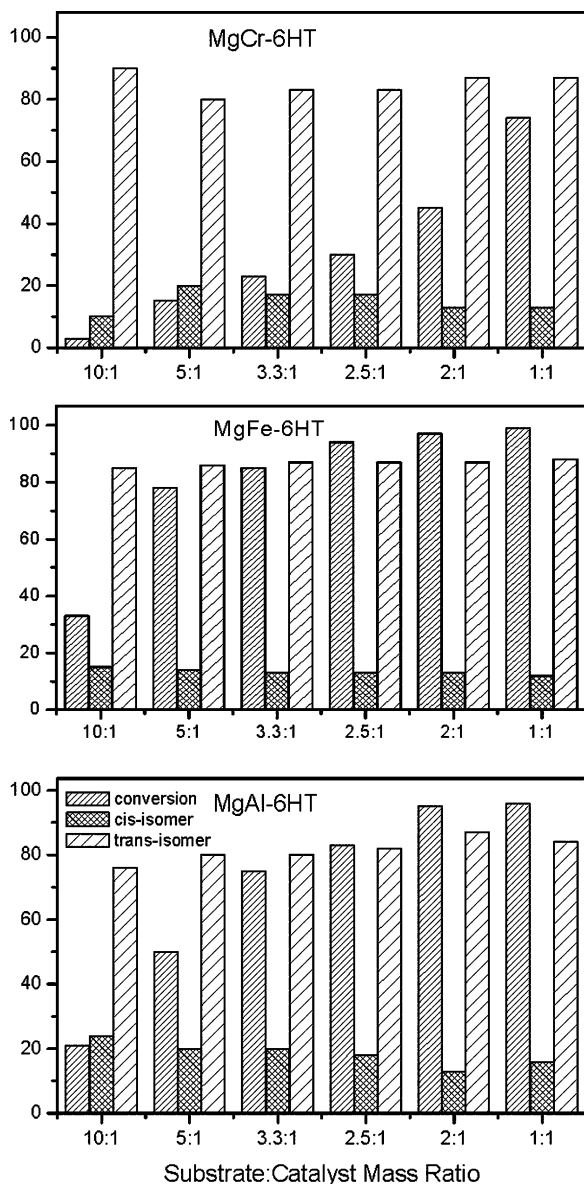


Fig. 3. Variation in conversion of safrole and selectivities of *cis*- and *trans*-isofafrole as a function of substrate:catalyst mass ratio over MgM(III)-6HT (substrate: 0.5 g; catalyst: 250 mg; reaction temperature/time 200 °C/6 h; solvent (DMSO): 10 ml).

catalysts with time, suggesting lack of inter conversion reactions.

A plausible reaction pathway for the isomerization of safrole over the catalyst surface is given in Scheme 1. The hydroxy group attached to Mg^{2+} may act as a Bronsted basic site in abstracting the proton of an active methylene group in the allylic moiety resulting in resonance stabilized carbanion. Subsequently, it combines with a proton resulting in thermodynamically preferred isomerized product. CO adsorption at low temperatures ($-196\text{ }^{\circ}\text{C}$) using FT-IR spectroscopy revealed the absence of Lewis basic sites for the sample calcined at 200 °C suggesting the non-involvement of such sites for this reaction under our experimental conditions [30].

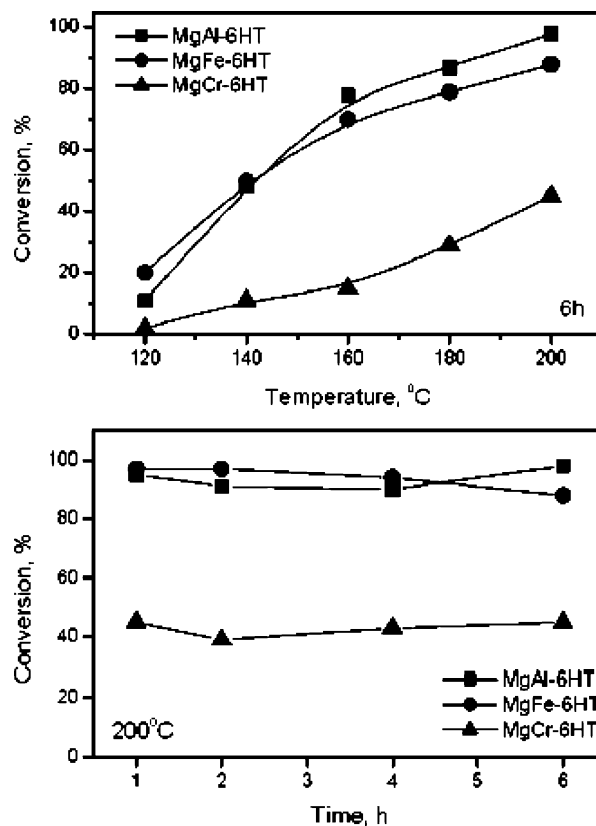
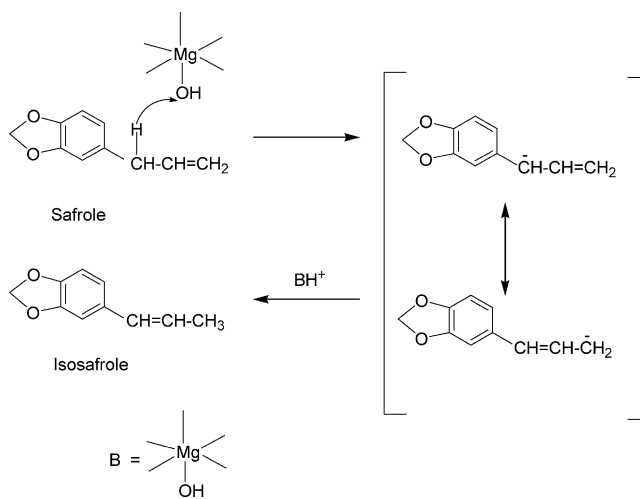


Fig. 4. Influence of reaction temperature and reaction time on the conversion of safrole over MgM(III)-6HT (substrate: 0.5 g; catalyst: 250 mg; solvent (DMSO): 10 ml).



Scheme 1. Reaction pathway for isomerization of safrole over MgM(III) hydroxalcite.

5. Conclusions

MgM(III) hydroxalcites where M(III) = Al, Fe and Cr were synthesized by coprecipitation under low supersaturation. Among the trivalent metal ions studied, Al offered maximum crystalline material followed by Fe and Cr. Thermal analysis for these materials indicated that the stability

varied with both M(II)/M(III) atomic composition as well as by the nature of trivalent metal ion. Isomerization of safrole was carried out over these materials, wherein it was enunciated that both end members showed poor activity, while materials crystallizing in HT-like network offered significant activity, which varied with both M(II)/M(III) atomic composition as well with trivalent metal ion. Among the catalysts studied, MgAl-6HT showed a conversion of 98% using a substrate:catalyst mass ratio of 2:1 using DMSO as solvent. Bronsted basic hydroxy groups attached to Mg²⁺ are probably the active centers involved in this isomerization reaction.

Acknowledgements

SK thanks Council of Scientific and Industrial Research, New Delhi, and Indian National Science Academy, New Delhi (BS/YSP-22) for financial assistance granted under Young Scientists Schemes. DK thanks Council of Scientific and Industrial Research (CSIR), New Delhi, for the award of senior research fellowship.

References

- [1] K. Bauer, D. Garbe, H. Surberg, Flavors and fragrances, in: Ullmann Encyclopedia of Industrial Chemistry, Electronic Release, 6th ed., 2002.
- [2] P. Gandilhon, United States Patent 4,138,411 (1979).
- [3] L. Cervený, A. Krejčíková, A. Marhoul, V. Ruzicka, React. Kinet. Catal. Lett. 33 (1987) 471.
- [4] N. Tsuneyuki, S. Gohu, F. Masami, United States Patent 3,852,305 (1974).
- [5] A.J. Birch, G.S.R. Subba Rao, Tetrahedron Lett. (1968) 3797.
- [6] S. Achyutha Rao, M. Periasamy, J. Organomet. Chem. 342 (1998) 15.
- [7] Y. Qian, G. Li, X. Zheng, Y.-Z. Huang, J. Mol. Catal. 78 (1993) L31.
- [8] A.S. Radhakrishna, S.K. Suri, K.R.K. Prasada Rao, K. Sivaprakash, B.B. Singh, Synth. Commun. 20 (1990) 345.
- [9] L.N. Thach, D.-L. Hanh, N. Ba Hiep, A.S. Radhakrishna, B.B. Singh, A. Loupy, Synth. Commun. 23 (1993) 1379.
- [10] L.N. Thach, T.H. Anh, N.A. Kiet, T.M. Phuong, Tap Chi Hoa Hoc 37 (1999) 92.
- [11] G.V. Salmoria, E.L. Dall'Oglio, C. Zucco, Synth. Commun. 27 (1997) 4335.
- [12] L.N. Thach, C.R. Strauss, J. Chem. 38 (2000) 76.
- [13] H. Hattori, Chem. Rev. 95 (1995) 527.
- [14] Y. Ono, T. Baba, in: J.J. Spivey (Ed.), "Catalysis"—Specialist Periodical Report, Royal Society of Chemistry, 2000, p. 1.
- [15] J. Weitkamp, M. Hunger, U. Ryma, Micropor. Mesopor. Mater. 48 (2001) 255.
- [16] M.J. Climent, A. Corma, S. Iborra, A. Velty, J. Mol. Catal. A 182–183 (2002) 327.
- [17] A. Beres, I. Palinko, I. Kiricsi, J.B. Nagy, Y. Kiyozumi, F. Mizukami, Appl. Catal. A 182 (1999) 237.
- [18] J.I. Di Cosimo, V.K. Diez, M. Zu, E. Iglesia, C.R. Apesteguia, J. Catal. 178 (1998) 499.
- [19] F. Trifirò, A. Vaccari, in: J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vogtle, J.-M. Lehn, G. Aberti, T. Bein (Eds.), Comprehensive Supramolecular Chemistry, Solid State Supramolecular Chemistry: Two- and Three-dimensional Inorganic Networks, vol. 7, Pergamon Press, Oxford, 1996, p. 251.
- [20] A. Dubey, S. Kannan, S. Velu, E. Suzuki, Appl. Catal. A 238 (2003) 319.
- [21] Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data, Pennsylvania, 1996 (set No. 46).
- [22] V. Rives, Ads. Sci. Technol. 8 (1991) 95.
- [23] J.M.C. Barriga, M.A. Ulibarri, F.M. Labajos, V. Rives, Chem. Mater. 9 (1997) 312.
- [24] E. Uzunova, D. Klissurski, I. Mitov, P. Stefanov, Chem. Mater. 5 (1993) 576.
- [25] S. Kannan, V. Rives, J. Mater. Chem. 10 (2000) 489.
- [26] S. Kannan, C.S. Swamy, J. Mater. Sci. 32 (1997) 1623.
- [27] R.D. Shannon, C.T. Mitchell, Acta Crystallogr., Sec. B 25 (1969) 925.
- [28] S. Kannan, S. Velu, V. Ramkumar, C.S. Swamy, J. Mater. Sci. 30 (1995) 1462.
- [29] D. Tichit, D. Latic, B. Coq, R. Durand, R. Teissier, J. Catal. 219 (2003) 167.
- [30] S. Kannan, D. Kishore, K. Hadjiivanov, H. Knozinger, Langmuir 19 (2003) 5742.