

# Solvent free aldol condensation of propanal to 2-methylpentenal using solid base catalysts

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## Abstract

Catalytic activities of alkali ion-exchanged zeolites, alumina, alkali treated alumina and hydrotalcite having varied Mg/Al molar ratio were evaluated for aldol condensation of propanal in liquid phase under solvent free conditions. The maximum conversion (97%) of propanal with 99% selectivity of 2-methylpentenal was obtained at 100 °C and 10 h using activated hydrotalcite of Mg/Al molar ratio of 3.5 as a catalyst. The basicity of the activated hydrotalcite of Mg/Al ratio 1.5, 2.5 and 3.5 was evaluated by isomerization of  $\beta$ -isophorone to  $\alpha$ -isophorone as a model test reaction reported for basicity measurement. The effect of amount of catalyst and temperature on the conversion of propanal, selectivity of 2-methylpentenal and initial rate of reaction were studied in detail. The activation energy for propanal condensation under solvent free condition was found to be 58 kJ using activated hydrotalcite of Mg/Al molar ratio 3.5 as a catalyst. The catalyst was recycled six times without any significant loss in conversion and selectivity.

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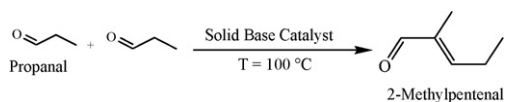
**Keywords:** Aldol condensation; Propanal; Cation exchanged zeolites; Hydrotalcite; Kinetics; 2-Methylpentenal

## 1. Introduction

2-Methylpentenal is a commercially important chemical that finds applications in pharmaceuticals, fragrances, flavors, cosmetics and as an intermediate for the synthesis of various pharmacologically active compounds [1]. Commercially, 2-methylpentenal is synthesized by the aldol condensation of propanal in the presence of liquid base like KOH or NaOH in stoichiometric amount [1–3]. Under optimum reaction conditions, 99% conversion of propanal is achieved with 86% selectivity of 2-methylpentenal using liquid base [1]. The existing process for the synthesis of 2-methylpentenal from propanal is not eco-friendly and have other drawbacks like the use of KOH or NaOH in higher than stoichiometric amount, lower selectivity, separation of spent KOH/NaOH from post-synthesis reaction mixture, effluent treatment and disposal of spent liquid base. Besides, the alkali metal hydroxides require large amount of water for the

neutralization and washing after the completion of reaction. It is desirable to find solid base catalysts which could substitute liquid bases and would still show the advantages of heterogeneous catalysis, i.e. ease of separation of the products, decreased corrosion of the reactor, and possible regeneration of the catalyst. Therefore, research efforts are directed to develop a catalytic process, which can produce 2-methylpentenal from propanal with high selectivity employing eco-friendly reusable solid base catalyst (Scheme 1). The synthesis of C<sub>6</sub> aldehydes from propanal via aldol condensation reaction in ionic liquid media with NaOH as a catalyst was studied by the Mehnert et al. The authors have reported 100% conversion of propanal with 83% selectivity for C<sub>6</sub> aldehydes at 80 °C in 3 h reaction time using [bdmim]PF<sub>6</sub> ionic liquid as solvent medium with sodium hydroxide as a catalyst [4]. Matsui et al. studied the effect of CO<sub>2</sub> pressure on the selectivity of condensation products in the presence of MgO with small amount of water. In the supercritical region, 94% selectivity of 2-methylpentenal was obtained near the critical pressure of 12 MPa [5]. The vapor phase aldol condensation of the propanal was studied by Scheidt, who reported higher than 95% selectivity of 2-methylpentenal by passing the vapors

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Scheme 1. Aldol condensation of propanal.

of propanal over heated lithium phosphate [6]. In another study, Tang et al. reported the synthesis of 2-methylpentenal with 94% yield from self-condensation of propanal using ion-exchanged resins in 2 h reaction time at 30 °C using benzene as a solvent [7].

Hydrotalcites (HT) and cation exchanged zeolites have recently received much attention as solid base catalysts [8–10]. Thermal decomposition of hydrotalcite at about 450 °C results into highly active uniformly mixed oxides, which is a potential solid base catalyst for a variety of organic transformations such as condensation, isomerization, anion exchangers and epoxidation reactions [11–15]. Numerous studies are reported on self-condensation of butanal, acetone, and cross condensation reactions using hydrotalcites or other solid base catalysts [16–23], but only limited literature is available on the self-condensation of propanal using solid base catalyst.

The aim of present investigation is to develop the suitable solid base catalyst for aldol condensation of propanal in solvent free environment. The various alkali ion-exchanged zeolites, alumina, alkali impregnated alumina and hydrotalcites were synthesized, characterized and their catalytic activities were evaluated for aldol condensation of the propanal. The study for the aldol condensation of propanal using hydrotalcite as a catalyst has not been reported to the best of our knowledge.

## 2. Experimental

### 2.1. Materials

The propanal and 2-methylpentenal were purchased from Sigma–Aldrich, USA and used without further purification. Zeolites powder (Si/Al = 1.25) procured from Zeolites and Allied Products, Mumbai, India, was used without any further purification. The chloride salts of cesium, potassium and rubidium were purchased from Sigma–Aldrich, USA. Magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium hydroxide (NaOH) were purchased from s.d. Fine Chemicals, India for synthesis of hydrotalcite samples. The double distilled milli-pore deionized water was used during synthesis of hydrotalcites.

### 2.2. Catalyst synthesis

The exchange of various alkali ions (cations) into the framework of the zeolites was carried out by reported procedure [12,24]. The alkali ion-exchanged zeolites Cs–X, Rb–X, K–X were prepared by four times ion-exchange of Na–X zeolite with 1M aqueous solution of corresponding salts of cesium, rubidium and potassium at 80 °C for 4 h. The resulting Cs–X, Rb–X and K–X were washed with deionized distilled water. The alkali ion-exchanged zeolite samples were dried in an oven at 110 °C for 12 h and activated for 4 h at 450 °C in a muffle furnace.

The impregnation of KOH on the surface of neutral alumina was carried out by the stirring of neutral alumina with 10, 20, 30, and 50% (by weight) solution of KOH at room temperature for 12 h. After 12 h, the solids were separated by the filtration, followed by drying overnight at 110 °C. The impregnated samples were activated at 450 °C for 4 h in a muffle furnace.

The hydrotalcite samples with Mg/Al molar ratio of 1.5 to 3.5 were synthesized by co-precipitation method at constant pH. Typically, for hydrotalcite sample with Mg/Al molar ratio = 2.5, an aqueous solution (A) of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.22 mol) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.088 mol) in 200 mL double distilled deionized water was prepared. The solution A was added dropwise into a second solution (B) containing NaOH (0.72 mol) and  $\text{Na}_2\text{CO}_3$  (0.21 mol) in 200 mL double distilled deionized water, in around 2 h under vigorous stirring at room temperature. The content was then transferred into the teflon coated stainless steel autoclave and aged at 70 °C for 12 h under autogenous water vapor pressure. After 14 h, the precipitate formed was filtered and washed thoroughly with hot distilled water until pH of the filtrate was 7. The washed precipitate was dried in an oven at 80 °C for 14 h. The hydrotalcite samples with varied Mg/Al molar ratio (1.5–3.5) were synthesized as per above procedure having appropriate amounts of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . The hydrotalcite samples of Mg/Al molar ratio from 1.5 to 3.5 were activated at 450 °C for 4 h in a muffle furnace. The solid material was then cooled and stored under vacuum prior to using those as catalysts for aldol condensation of propanal.

### 2.3. Characterization of the catalysts

Powder X-ray diffraction (P-XRD) patterns of alkali ion-exchanged zeolites, KOH treated alumina and hydrotalcite samples were recorded with Phillips X'Pert MPD system equipped with XRK 900 reaction chamber, using Ni-filtered  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) over a  $2\theta$  range of 2–70°. The FT-IR spectra of the hydrotalcite samples of different Mg/Al ratio were recorded from 400 to 4000  $\text{cm}^{-1}$  with a Perkin-Elmer Spectrum GX FT-IR system using KBr pellets. Thermogravimetric analysis (TGA) of the hydrotalcite samples was carried out using Mettler TGA/SDTA 851e equipment in flowing nitrogen or argon (flow rate, 50 mL/min), at a heating rate of 10 °C/min and the data were processed using Star<sup>e</sup> software. Scanning electron microscopy (SEM) images of the hydrotalcite samples were taken on a microscope (Leo Series VP1430, Germany) having silicon detector equipped with EDX facility (Oxford instruments). The samples were coated with gold using sputter coating to avoid charging. Analysis was carried out at an accelerating voltage of 15 kV.

### 2.4. Aldol condensation reaction

Typically, aldol condensation of propanal was carried out in a 50 mL oven dried double necked round bottom flask in which propanal and catalyst were taken with 0.01 g tetradecane as an internal standard. One neck of flask was fitted with 0.7 m long refluxing condenser having spiral tube inside and another neck

of flask was closed with silicon rubber septum. The top of the refluxing condenser was blocked by standard cork. The water at 15 °C was circulated in refluxing condenser constantly during the course of reaction from water chiller at flow rate of 6 L/min. The entire experimental setup was kept in an oil bath equipped with temperature and agitation speed controlling unit. The reaction was carried out at 100 °C for 10 h. The reaction mixture was cooled to room temperature after set reaction time and was subjected to filtration. The silicon grease was used in all joints to prevent vapor loss of propanal and conversion of propanal was calculated by internal standard method. However, the weight of initial reaction mixture and product mixture after the completion of reaction was compared to ensure absence of vapor loss of propanal. For the kinetic studies, 5 g propanal with 0.5 g catalyst were taken and samples (0.01 mL) were withdrawn during the experiment by glass syringe at different time intervals. The analysis of product mixture was carried out by gas chromatography (GC) (Shimadzu 17A, Japan) and GC–MS (mass spectrophotometer, Shimadzu-QP2010, Japan). The GC has a 5% diphenyl and 95% dimethyl siloxane universal capillary column (60 m length and 0.25 mm diameter) and a flame ionization detector (FID). The initial column temperature was increased from 40 to 200 °C at the rate of 10 °C/min. Nitrogen gas was used as the carrier gas. The temperatures of the injection port and FID were kept constant at 200 °C during product analysis. The retention time of different compounds was determined by injecting a pure compound under identical gas chromatography conditions.

### 2.5. Isomerization of $\beta$ -isophorone

The isomerization of  $\beta$ -isophorone to  $\alpha$ -isophorone was performed as a model test reaction for basicity measurement of activated hydrotalcite [13,25]. 10 mL of  $\beta$ -isophorone was added into 30 mL heptane as a solvent in a 50 mL oven dried double necked round bottom flask. The reaction mixture was kept at 35 °C temperature. The nitrogen was purged to remove CO<sub>2</sub> present in the reaction atmosphere and agitation was started at 1000 rpm. After 2 min, 0.1 g catalyst was added to this mixture from side neck of the round bottom flask and reaction was continued by stirring at 1000 rpm. The analysis of product mixture was carried out by GC–MS (mass spectrometer, Shimadzu-QP2010, Japan).

### 2.6. Kinetic analysis and reproducibility

The parameters, which might have pronounced effect on the rate of aldol condensation of propanal include, concentration of reactant, amount of catalyst and reaction temperature. Therefore, the kinetic experiments were carried out by varying these parameters. In each case, the change in concentration of reactant was determined by gas chromatography at fixed time intervals. The initial rate of reaction was calculated by the method reported in literature [26] in the lower conversion (5–8%) range of propanal. The mass transfer resistance was analyzed by performing the primary experiments at varied amount of catalyst and stirring speed. In the present experimental conditions, 2-methylpentenal and 3-hydroxy-2-methylpentanal were the only major products

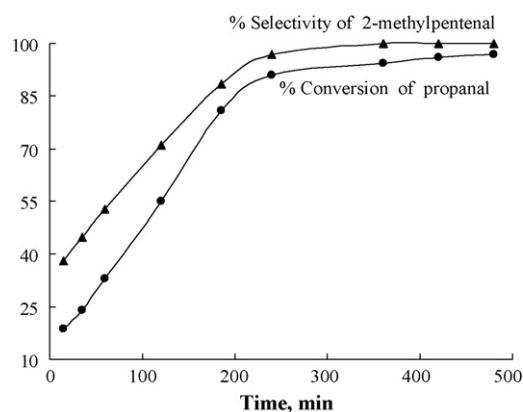


Fig. 1. Concentration–time profile for aldol condensation of propanal.

observed to form in the aldol condensation of propanal. However, formation of 3-pentanone in small amount cannot be ignored in some experimental conditions during the course of aldol condensation of propanal.

To ensure the reproducibility of aldol condensation of propanal, repeated experiments were carried out under identical reaction conditions. The results obtained, including conversions and selectivities were found to be reproducible within less than 7% variation, confirming the reproducibility of the results. A typical concentration profile of reactant consumption and product formation is shown in Fig. 1. The conversion of propanal and selectivity of 2-methylpentenal was observed to increase linearly upto 3.5 h. Slow rate of increment in the conversion and selectivity was seen upto 6 h and it attains saturation on further increase in the reaction time.

## 3. Results and discussion

### 3.1. Catalyst characterization

The P-XRD patterns of alkali ion-exchanged zeolites and KOH impregnated on neutral alumina are shown in Figs. 2 and 3. The powder XRD profiles of original and modified zeolite samples showed all the characteristic peaks of zeolites structure closely matching with the reported reflections for highly crystalline zeolite Na–X at  $2\theta$  values 6.1°, 10.0°, 15.5°, 20.1°, 23.9°, 26.7°, 29.4°, 30.7°, 31.0°, 33.5°, 36.8° and 42.4° (Fig. 2). The

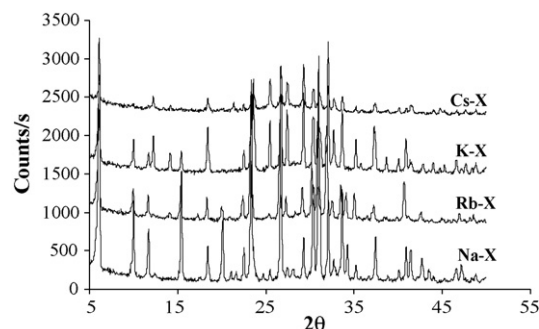


Fig. 2. P-XRD patterns of alkali ion-exchanged zeolites.

Table 1  
Chemical composition and crystallinity of catalysts used

Catalyst samples	Chemical composition	% Crystallinity	Surface area (m <sup>2</sup> /g)
Na-X	Na <sub>88</sub> Al <sub>88</sub> Si <sub>104</sub> O <sub>384</sub>	100	542
K-X	K <sub>88</sub> Al <sub>88</sub> Si <sub>104</sub> O <sub>384</sub>	91	496
Rb-X	Rb <sub>84</sub> Na <sub>4</sub> Al <sub>88</sub> Si <sub>104</sub> O <sub>384</sub>	88	476
Cs-X	Cs <sub>76</sub> Na <sub>12</sub> Al <sub>88</sub> Si <sub>104</sub> O <sub>384</sub>	62	245
HT(1.5)	[Mg <sub>0.6</sub> Al <sub>0.4</sub> (OH) <sub>2</sub> ](CO <sub>3</sub> ) <sub>0.20</sub> ·0.84H <sub>2</sub> O	94	58
HT(2.0)	[Mg <sub>0.6</sub> Al <sub>0.4</sub> (OH) <sub>2</sub> ](CO <sub>3</sub> ) <sub>0.20</sub> ·0.81H <sub>2</sub> O	100	62
HT(2.5)	[Mg <sub>0.72</sub> Al <sub>0.28</sub> (OH) <sub>2</sub> ](CO <sub>3</sub> ) <sub>0.14</sub> ·0.6H <sub>2</sub> O	88	67
HT(3.0)	[Mg <sub>0.75</sub> Al <sub>0.25</sub> (OH) <sub>2</sub> ](CO <sub>3</sub> ) <sub>0.125</sub> ·0.76H <sub>2</sub> O	77	69
HT(3.5)	[Mg <sub>0.78</sub> Al <sub>0.22</sub> (OH) <sub>2</sub> ](CO <sub>3</sub> ) <sub>0.11</sub> ·0.58H <sub>2</sub> O	72	75
Alumina	Al <sub>2</sub> O <sub>3</sub>		180
10% KOH on alumina	10% KOH on Al <sub>2</sub> O <sub>3</sub>		132
20% KOH on alumina	20% KOH on Al <sub>2</sub> O <sub>3</sub>		59
30% KOH on alumina	30% KOH on Al <sub>2</sub> O <sub>3</sub>		32
50% KOH on alumina	50% KOH on Al <sub>2</sub> O <sub>3</sub>		7

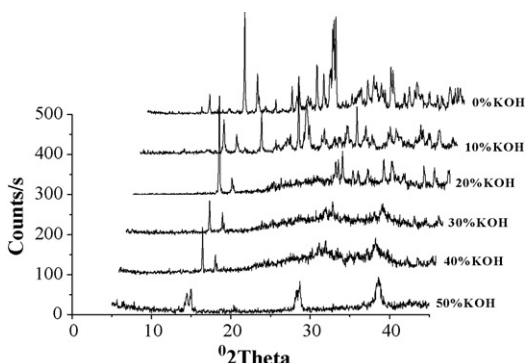


Fig. 3. P-XRD patterns of KOH treated neutral alumina.

percentage crystallinity of the alkali ion-exchanged zeolites was observed to decrease as compared to zeolite Na-X (Table 1).

The P-XRD pattern of pure alumina shows the maximum crystallinity and is considered as 100% crystalline material for the comparison of crystallinity after impregnation of KOH (Fig. 3). It was observed that the crystallinity of the impregnated alumina decreased significantly on increasing the amount of KOH. The alumina became almost amorphous after impregnation of 30% KOH on the surface of neutral alumina.

The P-XRD patterns of as-synthesized hydrotalcite [HT(3.5)] and activated hydrotalcite [HT(3.5)-A] are shown in Fig. 4.

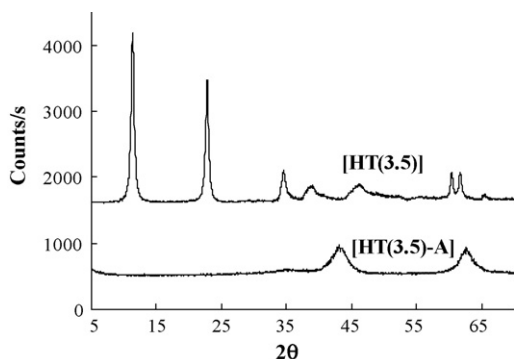


Fig. 4. P-XRD patterns of [HT(3.5)] and [HT(3.5)-A].

The P-XRD patterns of as-synthesized hydrotalcite showed sharp, intense and symmetric peaks at lower diffraction angles ( $2\theta = 10\text{--}25^\circ$ ) and broad asymmetric reflections at higher diffraction angles ( $2\theta = 30\text{--}50^\circ$ ), which are characteristics of highly crystalline layered structure. The percentage crystallinity of the hydrotalcite samples was calculated by comparing the summation of integral intensities of 003 ( $2\theta = 10.5^\circ$ ) and 006 ( $2\theta = 23.3^\circ$ ) planes and the sample with maximum intensity [HT(2.5)] was considered as a 100% crystalline material. The crystallinity of hydrotalcite samples decreased with increase in Mg/Al molar ratio. The decrease in the crystallinity on increasing Mg/Al molar ratio of hydrotalcite samples is due to increase in amount of divalent cation ( $\text{Mg}^{2+}$ ) which have ionic radii  $0.65 \text{ \AA}$  that favors the formation of brucite by replacing the smaller ionic radii trivalent cations ( $\text{Al}^{3+}$ ) [27,28]. The P-XRD patterns of [HT(3.5)-A] consist of broadened peaks that can be assigned to a Mg–Al mixed oxide phase, with diffraction lines at values very similar to that of MgO.

The FT-IR spectra of [HT(3.5)] and [HT(3.5)-A] are shown in Fig. 5. The absorption at  $3450\text{--}3550 \text{ cm}^{-1}$ , present in all hydrotalcite samples is due to H-bonding stretching vibrations of OH group in the brucite-like layer. The shoulder present at around  $3000 \text{ cm}^{-1}$  is attributed to hydrogen bonding between water molecules and interlayer  $\text{CO}_3^{2-}$  anions. The appearance of the shoulder at  $1650 \text{ cm}^{-1}$  is the characteristic band of  $\text{H}_2\text{O}$ . The

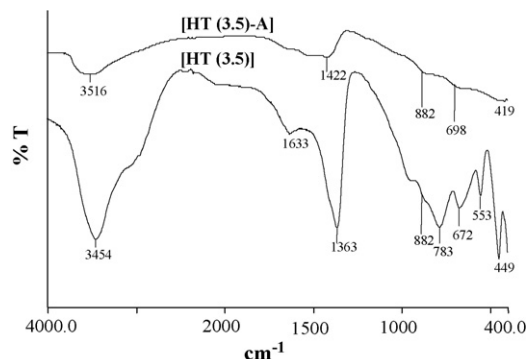


Fig. 5. FT-IR spectra of [HT(3.5)] and [HT(3.5)-A].

asymmetric stretching,  $\nu_3$ , appeared around  $1380\text{ cm}^{-1}$  could be assigned to interlayer carbonates, confirming the formation of Mg–Al hydrotalcite with intercalated carbonate anions. The low frequency region showed bands at about  $550$ ,  $790$ ,  $940\text{ cm}^{-1}$ , corresponding to the Al–O and the band at  $635\text{ cm}^{-1}$  is assigned to Mg–O [27]. Calcination of hydrotalcite shows that the water molecules have been removed and this is evidenced by the disappearance of the bands at  $1650\text{ cm}^{-1}$  (water bending vibrations), and around  $3000\text{ cm}^{-1}$  (interaction of  $\text{H}_2\text{O}-\text{CO}_3^{2-}$  in the interlayer). The intensity of the band at  $3450\text{--}3550\text{ cm}^{-1}$  also decreases significantly due to de-hydroxylation. The disappearance of vibration assigned to interlayer carbonates at around  $1380\text{ cm}^{-1}$  was observed in the activated hydrotalcite samples.

TGA curves of [HT(3.5)] and [HT(3.5)-A] are shown in Fig. 6. The TGA profiles are in good agreement with those available in the literature for the hydrotalcite [8]. The SEM images were recorded to observe the effect of activation on the morphology of the as-synthesized hydrotalcite. SEM images of [HT(3.5)] and [HT(3.5)-A] are shown in Fig. 7. The micrographs of all hydrotalcites show well-developed layers with platelet structure. The morphology of Mg–Al mixed oxides obtained upon calcination seems to be similar to that of as-synthesized hydrotalcite.

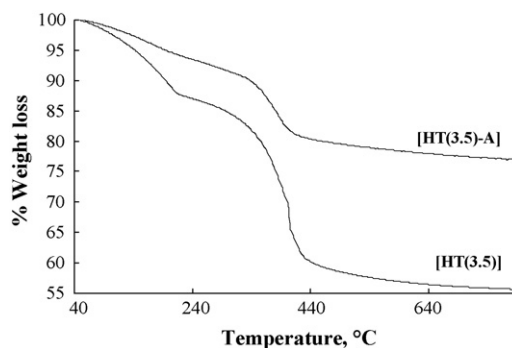


Fig. 6. TGA of [HT(3.5)] and [HT(3.5)-A].

### 3.2. Catalytic activity for the aldol condensation of propanal

The conversion of propanal varied from 22–42% with 92–94% selectivity of 2-methylpentenal using various alkali ion-exchanged zeolites without any thermal treatment or activation (Table 2, entries 1–4), which are known to be weak bases. On the activation of ion-exchanged zeolites at  $450\text{ °C}$  for 4 h, the conversion of propanal decreased with increase in the selectivity of 2-methylpentenal (Table 2, entries 5–8). The Zeolite

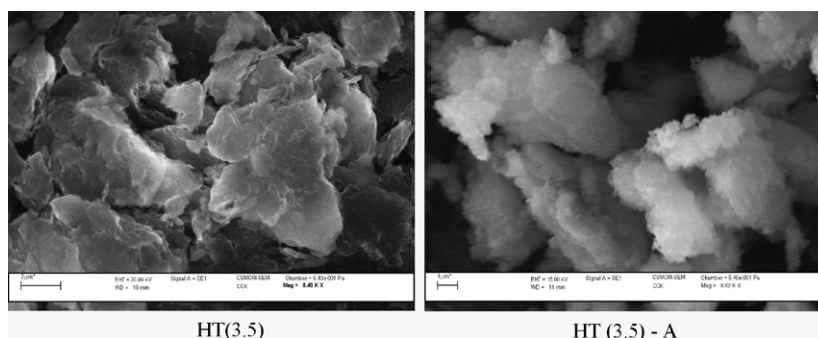


Fig. 7. SEM images of [HT(3.5)] and [HT(3.5)-A].

Table 2  
Aldol condensation of propanal using various solid base catalysts

Entry	Catalysts	Activation temperature/time	% Conversion	% Selectivity	
				2-Methylpentenal	3-Hydroxy-2-methylpentanal
1	Cs–X	Without act.	42	94	6
2	Rb–X	Without act.	35	94	6
3	K–X	Without act.	27	95	5
4	Na–X	Without act.	22	92	8
5	Cs–X	$450\text{ °C}/4\text{ h}$	38	99	1
6	Rb–X	$450\text{ °C}/4\text{ h}$	30	98	2
7	K–X	$450\text{ °C}/4\text{ h}$	26	98	2
8	Na–X	$450\text{ °C}/4\text{ h}$	19	97	3
9	Alumina-neutral	Without act.	42	97	3
10	Alumina-neutral	$450\text{ °C}/4\text{ h}$	46	97	3
11	10% KOH on alumina	Without act.	21	98	2
12	20% KOH on alumina	Without act.	17	98	2
13	30% KOH on alumina	Without act.	15	97	3
14	50% KOH on alumina	Without act.	12	96	4

Reaction conditions: propanal = 1.0 g, catalyst = 0.1 g, *n*-decane (internal standard) = 0.01 g, temperature =  $100\text{ °C}$ , reaction time = 10 h.

Table 3  
Aldol condensation of propanal using as-synthesized and activated hydrotalcites of Mg/Al molar ratio 1.5 to 3.5

Entry	Catalysts	Activation temperature/time	% Conversion	% Selectivity		
				2-Methylpentenal	3-Hydroxy-2-methylpentanal	3-Pentanone
1	HT (1.5)	Without act.	40	48	52	–
2	HT (2.0)	Without act.	45	52	48	–
3	HT (2.5)	Without act.	52	80	17	3
4	HT (3.0)	Without act.	58	83	15	2
5	HT (3.5)	Without act.	83	86	9	5
6 <sup>a</sup>	Ni–Mg–Al	Without act.	66	98	–	2
7	HT (1.5)	450 °C/4 h	44	68	30	2
8	HT (2.0)	450 °C/4 h	47	83	17	–
9	HT (2.5)	450 °C/4 h	80	92	8	–
10	HT (3.0)	450 °C/4 h	86	96	4	–
11	HT (3.5)	450 °C/4 h	97	99	–	1
12 <sup>a</sup>	Ni–Mg–Al	450 °C/4 h	90	97	2	1

Reaction conditions: propanal = 1.0 g, catalyst = 0.1 g, *n*-decane (internal standard) = 0.01 g, temperature = 100 °C, reaction time = 10 h.

<sup>a</sup> Mg/Al = 3.0.

X has pore opening of 7.4 Å and pore cavity of 11.8 Å. The molecular dimensions of *n*-propanal and 2-methylpentenal are 4.6 and 6.7 Å, respectively, which are smaller than the pore opening diameter of zeolite. Therefore, the effect of microporosity was excluded in the present study. The results obtained using alkali ion-exchanged zeolites as catalysts indicate that the aldol condensation of propanal depends on the type of alkali metal ion exchanged into zeolite cage. The conversions obtained follow the order Cs–X > Rb–X > K–X > Na–X which is in agreement with the order of basicity reported in the literature for these solids [29,30]. The overall basicity of the alkali ion-exchanged zeolites depends upon the nature of extra-framework cations and presence of less polarizable cations. The less polarizable cations such as cesium or rubidium resulted into more basic zeolites as compared to those formed by sodium or lithium exchange [31]. This is also supported by the calculation of average partial charge on oxygen atom using Sanderson electronegativity methods for Cs–X, Rb–X, K–X, Na–X [32]. These were observed to be –0.45, –0.44, –0.43, –0.41, respectively, indicating the basicity order of zeolites as Cs–X > Rb–X > K–X > Na–X [12].

Conversion of propanal was found to be 42% with 97% selectivity of 2-methylpentenal using neutral alumina without activation. The conversion increased upto 46% with neutral alumina activated at 450 °C for 4 h (Table 2, entries 9 and 10). The conversion of propanal strongly depends on the amount of impregnated KOH on the neutral alumina (Table 2, entries 11–14). It decreases significantly (42–21%) on impregnation of 10% KOH on the surface of neutral alumina. Conversion data for different percentage of KOH impregnated alumina showed that lower the KOH impregnation, higher is the conversion and selectivity for propanal condensation. The surface area of the alumina samples decreased on increasing the amount of KOH (Table 1). This could be due to pore blocking of alumina on impregnation of KOH. The formation of potassium aluminate is also expected by the reaction of alumina with KOH. The KOH molecules are expected to be well dispersed on alumina surface at lower impregnation. However, with increased KOH impregnation, the poor KOH dispersion and lower surface area was obtained, hence

lower catalytic activity for the aldol condensation of propanal was observed in the present study.

The catalytic activity of as-synthesized and activated hydrotalcites of Mg/Al molar ratio from 1.5 to 3.5 was evaluated for the aldol condensation of propanal (Table 3) at 100 °C for 10 h. The conversion of propanal was found to increase from 40 to 83% with increase in the Mg/Al molar ratio of hydrotalcite from 1.5 to 3.5 without any activation (Table 3, entries 1–5). The selectivity of 2-methylpentenal was also observed to increase from 48 to 86% on increasing Mg/Al ratio of the as-synthesized hydrotalcite. The conversion and selectivity of aldehyde increased significantly on activation of as-synthesized hydrotalcite at 450 °C for 4 h under identical reaction conditions (Table 3, entries 7–11). The maximum conversion of propanal was observed to be 83% with selectivity of aldehyde 86% in case of as-synthesized hydrotalcite of Mg/Al molar ratio of 3.5, which increased upto 97% with 99% selectivity of 2-methylpentenal using activated hydrotalcite (Mg/Al = 3.5) as a catalyst. The Ni–Mg–Al was also observed to be more effective catalyst for aldol condensation of propanal as compared to the binary hydrotalcite of Mg/Al molar ratio 3.0. The 66% conversion of the propanal with 98% selectivity of the 2-methylpentenal was observed in reaction catalyzed by as-synthesized Ni–Mg–Al hydrotalcite (Table 3, entry 6). However, conversion of propanal increased upto 90% with 97% selectivity of 2-methylpentenal using activated Ni–Mg–Al hydrotalcite at 450 °C for 4 h (Table 3, entry 12).

For any base catalyzed reaction, maximum catalytic activity occurs at an optimum Mg/Al molar ratio and depends upon the base strength required to activate the particular reactant molecule. The increase in the conversion of propanal and selectivity of 2-methylpentenal with increasing Mg-content in hydrotalcite is explained in terms of increased basicity of hydrotalcite which aids aldol condensation reaction. The basicity of the as-synthesized hydrotalcite is mainly due to their hydroxyl functions and it can be adjusted by either changing the Mg/Al molar ratio of hydrotalcite or selection of suitable anion in the interlayer. In the present study, the observed increase in

Table 4  
Effect of reactant to catalyst ratio (by weight) on conversion and selectivity

Entry	Catalyst (mg)	% Conversion	% Selectivity		
			2-Methylpentenal	3-Hydroxy-2-methylpentanal	3-Pentanone
1	0.02	40	73	27	–
2	0.04	51	82	18	–
3	0.05	63	85	15	–
4	0.07	85	88	10	2
5	0.08	96	96	2	2
6	0.10	97	99	–	1
7	0.13	97	100	–	–
8	0.20	97	100	–	–

Reaction conditions: propanal = 1.0 g, *n*-decane (internal standard) = 0.01 g, temperature = 100 °C, time = 10 h.

conversion of propanal and selectivity of 2-methylpentenal on increasing the Mg/Al molar ratio of hydrotalcite samples is due to increment in basic character of hydrotalcite as discussed above. Two types of basic sites are identified in hydrotalcite, one weaker Bronsted OH<sup>−</sup> and second, stronger Lewis O<sup>2−</sup> sites [8]. At 450 °C, as-synthesized hydrotalcite converts into well dispersed mixture of magnesium and aluminium mixed oxides with high surface area and strong Lewis basic sites (isolated O<sup>2−</sup> anions), Mg<sup>2+</sup>–O<sup>2−</sup> pairs and weakly basic sites (hydroxide groups) on the surface [33]. The activated hydrotalcite is more basic as compared to as-synthesized hydrotalcite, both in terms of basic strength and number of basic sites [34]. The basic properties of activated hydrotalcite also depend upon the Mg/Al molar ratio. The basicity of the activated hydrotalcite of Mg/Al ratio 1.5, 2.5 and 3.5 was evaluated by isomerization of β-isophorone to α-isophorone as a model test reaction reported for basicity measurement [13,25]. The initial rate of reaction was observed to increase on increasing Mg/Al molar ratio of hydrotalcite (Fig. 8). The initial rate of reaction was calculated as  $37 \times 10^{-4}$  mol/(g<sub>cat</sub> s) for activated hydrotalcite of Mg/Al molar ratio 1.5 and increased upto  $48 \times 10^{-4}$  mol/(g<sub>cat</sub> s) for Mg/Al molar ratio 3.5. The initial rate of the reaction for the isophorone isomerization is reproducible within ±4% variation. The β-isophorone to α-isophorone is zero order; hence, the value of initial rate of reaction is equal to the rate constant. The value of rate constant for isophorone isomerization is proportional to the number basic sites [25]. The increasing Al content in the activated hydrotalcite resulted into decrease in total number

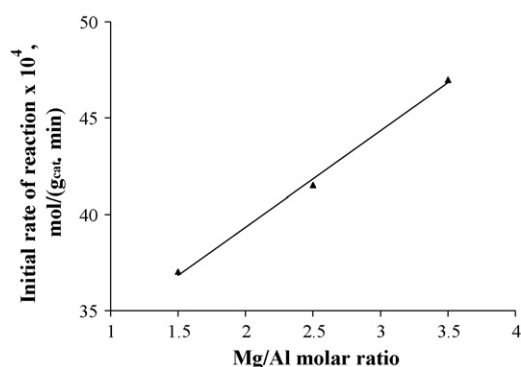


Fig. 8. Initial rate of reaction for the isomerization of β-isophorone to α-isophorone as a model reaction to test the basicity of [HT(3.5)-A].

of basic sites. Thus, higher Mg/Al molar ratio in the activated hydrotalcite gives the higher basicity and maximum catalytic activity.

Among the studied alkali ion-exchanged zeolites, alumina and KOH impregnated alumina, as-synthesized and activated hydrotalcites, the best conversion and selectivity were obtained using activated hydrotalcite for aldol condensation of propanal. Therefore, further studies for aldol condensation of propanal were carried out using activated hydrotalcite of Mg/Al molar ratio of 3.5 [HT(3.5)-A] as a catalyst. The effect of reactant to catalyst ratio and temperature on the conversion of propanal, selectivity of 2-methylpentenal and rate of condensation reaction were studied in details.

### 3.3. Effect amount of catalyst

The effect of amount of catalyst on the conversion, selectivity of 2-methylpentenal and rate of reaction was studied by varying the amount of catalyst at constant amount of propanal at 100 °C reaction temperature. At lower amount of catalyst, the lower conversion of propanal was observed (Table 4). For example, at 0.02 g catalyst, 40% conversion of propanal was obtained, which increased upto 63% on increasing the amount of catalyst to 0.05 g. However, further increase in the amount to 0.1 g, the conversion of the propanal increased upto 97%. The conversion of propanal was found to remain constant on further increase in the amount of catalyst. The selectivity of the 2-methylpentenal also followed the similar trend. The maximum selectivity (100%) of 2-methylpentenal was observed in the range of 0.1–0.2 g catalyst.

The effect of amount of catalyst on initial rate of reaction is given in Fig. 9. The initial rate of reaction was observed to increase on increasing the amount of catalyst. The amount of catalyst was varied from 0.02 to 2 g to study its effect on initial rate of reaction. Initially the rate of reaction was calculated as  $17 \times 10^{-4}$  mol/(g<sub>cat</sub> s) at 0.02 g catalyst. The rate of reaction increased linearly upto 0.1 g amount of catalyst. On further increase in the amount of catalyst upto 2 g, the slightly increase in the initial rate of reaction was observed. This indicates that the reaction is in kinetic region at 0.1 g of catalyst amount and mass transfer resistance can be neglected. The higher conversion and initial rate of reaction at higher amount of catalyst is due to the availability of sufficient amount of strong basic sites on

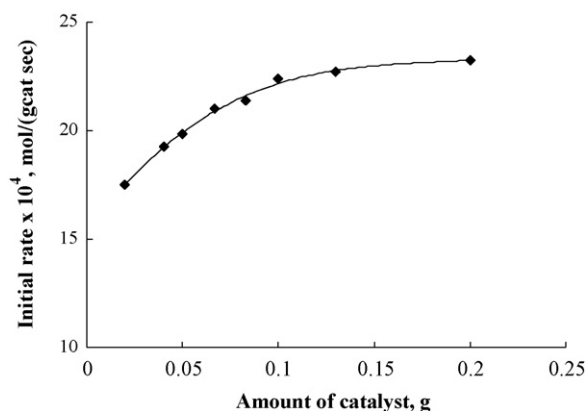


Fig. 9. Effect of amount of catalyst on initial rate of reaction.

the surface of activated hydrocalcite, which is used as a catalyst. As the amount of catalyst decreases, the amount of active basic sites present for condensation reaction on the surface of catalyst also decreases and hence lower catalytic activity was observed at higher reactant to catalyst ratio. Another possible reason for lower activity of the catalyst is strong adsorption of reactant molecules (or slow diffusion) on the surface of activated hydrocalcite at lower amount of catalyst, these could block the active basic sites present on the surface of catalyst for condensation reaction.

### 3.4. Effect of temperature

The effect of temperature on aldol condensation of propanal was studied by varying the reaction temperature from 45 to 100 °C at constant amount of propanal and activated hydrocalcite of Mg/Al molar ratio of 3.5 as catalyst (Table 5). The higher conversion of propanal (97%) with 99% selectivity of 2-methylpentenal was observed at 100 °C. The reaction kinetics was also observed to be significantly influenced by the reaction temperature (Fig. 10a). The effect of reaction temperature on the initial rate of reaction is shown in the Fig. 10b. The initial rate of reaction was found to increase linearly with increase in the reaction temperature. The initial rate of reaction was calculated as  $3.7 \times 10^{-4}$  mol/(g<sub>cat</sub> s) at 40 °C, which increased upto  $16.4 \times 10^{-4}$  mol/(g<sub>cat</sub> s) at 80 °C. On further increasing the temperature to 100 °C, the rate of reaction was found to be  $22.5 \times 10^{-4}$  mol/(g<sub>cat</sub> s). The activation energy for

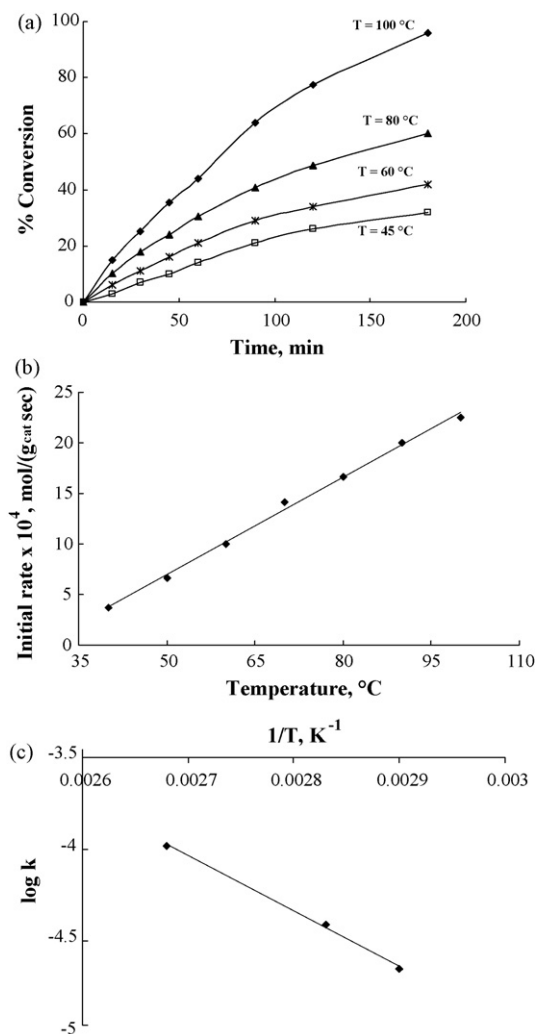


Fig. 10. (a) Effect of reaction temperature on conversion with respect to time. (b) Effect of reaction temperature on initial rate of reaction. (c) Arrhenius plot.

the propanal condensation is calculated by plotting the  $\log k$  versus  $1/T$  (Arrhenius plot, Fig. 10c) and found to be 58 kJ. The calculated activation energy in the present study was not observed in the range of 8–25 kJ, which again indicates that the reaction is far away from the diffusional (mass transfer) limitations.

The low activity of the catalyst for aldol condensation of propanal at lower temperature is due to the strong adsorption

Table 5  
Effect of reaction temperature on conversion and selectivity

Entry	T (°C)	% Conversion	% Selectivity		
			2-Methylpentenal	3-Hydroxy-2-methylpentanal	3-Pentanone
1	45	43	69	31	–
2	50	56	78	22	–
3	60	60	84	14	2
4	70	77	85	13	2
5	80	81	88	9	3
6	90	95	93	4	3
7	100	97	99	–	1

Reaction conditions: propanal = 1.0 g, catalyst (Mg/Al = 3.5, activated) = 0.1 g, *n*-decane (internal standard) = 0.01 g, time = 10 h.



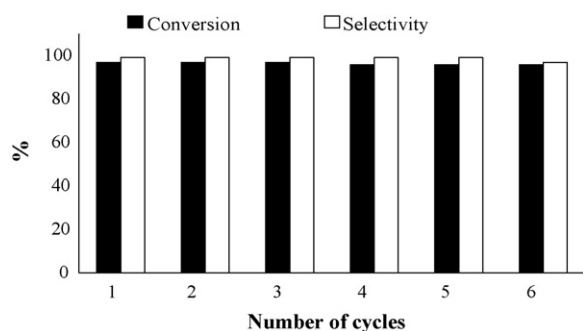


Fig. 11. Reusability of the catalyst.

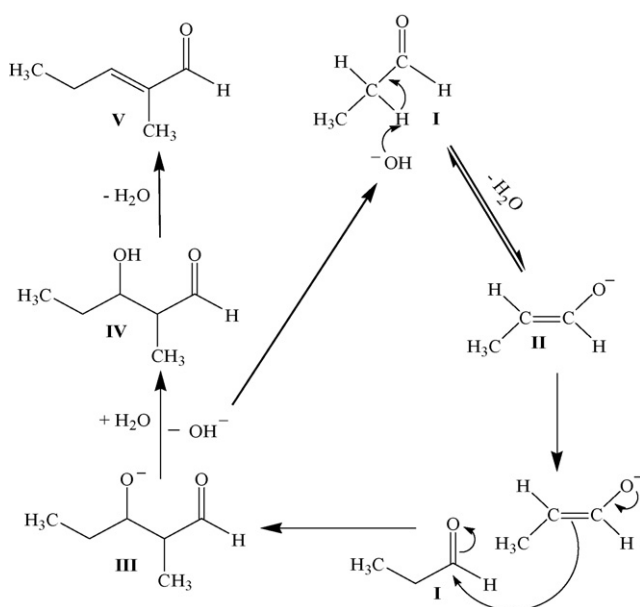
of propanal molecules on the surface of HT [35]. Therefore, high temperature is required to avoid this undesirable adsorption which leads to decreased catalytic activity.

### 3.5. Reusability of catalyst

The spent catalyst was regenerated in air flow at 450 °C for 4 h. The regenerated catalyst was used for the aldol condensation of the propanal under conditions similar to those used for the activated hydrotalcite of Mg/Al molar ratio of 3.5. From the data on conversion of propanal and selectivity of 2-methylpentenal given in Fig. 11, it is observed that the catalyst was reproducible upto six cycles without any significant loss in its activity for aldol condensation of propanal.

### 3.6. Reaction mechanism

The proposed mechanism for the aldol condensation of propanal catalyzed by hydrotalcite is shown in Scheme 2. The aldol condensation of the propanal is a three steps reaction. The OH<sup>-</sup> species present on the surface of hydrotalcite abstracts an



Scheme 2. Proposed reaction mechanism for aldol condensation of propanal using hydrotalcites as solid base catalyst.

acidic proton from  $\alpha$ -carbon of propanal (I) in first step to form a stabilized enolate (II). In the second step, formation of 2-methyl-1-oxo-pentan-3-ol anion (III) takes place by the nucleophilic addition of  $\alpha$ -carbon of enolate anion to the carbonyl group of another propanal. The resulting 2-methyl-1-oxo-pentan-3-ol anion (III) reacts with water to form the product of aldol addition (IV; 3-hydroxy-2-methylpentanal) and release the OH<sup>-</sup> species. Dehydration of the 3-hydroxy-2-methylpentanal (IV) to 2-methylpentenal (V), i.e.  $\alpha$ ,  $\beta$  unsaturated aldehyde occurs in the third step. The species OH<sup>-</sup> present on the hydrotalcite surface efficiently acts as Bronsted basic sites in the presence of water and provides a highly hydrophilic environment for aldol condensation of propanal [36].

## 4. Conclusions

The higher conversion of propanal was observed using hydrotalcite as a catalyst among the various studied solid base catalysts namely, alkali ion-exchanged zeolites, alumina, alkali treated alumina and hydrotalcite of varied Mg/Al molar ratio. The conversion and selectivity of 2-methylpentenal increased with increasing Mg/Al molar ratio of hydrotalcite. 97% conversion of propanal with 99% selectivity of 2-methylpentenal was achieved using [HT(3.5)-A]. From the kinetic data for aldol condensation of propanal, the initial rate of reaction was observed to increase on increasing the amount of catalyst upto 0.1 g, on further increase in the amount of catalyst, the initial rate of reaction was not changed significantly. The reaction kinetics was also observed to be significantly influenced by the reaction temperature. The activation energy for the propanal condensation was calculated by Arrhenius plot and found to be 58 kJ. The catalyst was recycled upto six cycles without any significant loss in its activity for aldol condensation of propanal.

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## References

- [1] A.D. Godwin, R.H. Schlosberg, F. Hershkowitz, M.G. Maturro, G. Kiss, K.C. Nadler, P.L. Buess, R.C. Miller, P.W. Allen, H.W. Deckman, R. Caers, E.J. Mozeleski, R.P. Reynolds, US 6,307,093 B1 (2001).
- [2] W. Schoenlebe, H. Hoffmann, W. Lengsfeld, DE 2,727,330 (1979).
- [3] P.Y. Blanc, A. Perret, F. Teppa, Helv. Chim. Acta 47 (1964) 567.
- [4] C.P. Mehnert, N.C. Dispenziere, R.H. Schlosberg, US 0,050,512 A1 (2003).
- [5] K. Matsui, H. Kawanami, Y. Ikushima, H. Hayashi, Chem Commun. (2003) 2502.
- [6] F.M. Scheidt, J. Catal. 3 (1964) 372.
- [7] S.P. Tang, H.Q. Li, D.L. Yin, Hunan Shifan Daxue Ziran Kexue Xuebao 24 (2001) 42.
- [8] F. Cavani, F. Trifiro, A. Vaccari, Catal. Today 11 (1991) 173.
- [9] G.J. Kelly, F. King, M. Kett, Green Chem. 4 (2002) 392.

- [10] J. Weitkamp, M. Hunger, U. Ryma, *Micropor. Mesopor. Mater.* 48 (2001) 255.
- [11] J.C.A.A. Roelofs, D.J. Lensveld, A.J. van Dillen, K.P. de Jong, *J. Catal.* 203 (2001) 184.
- [12] V.K. Srivastava, H.C. Bajaj, R.V. Jasra, *Catal. Commun.* 4 (2003) 543.
- [13] F. Figueras, J. Lopez, J. Sanchez-Valente, T.T.H. Vu, J.M. Clacens, J. Palomeque, *J. Catal.* 211 (2002) 144.
- [14] M.A. Ulibarri, I. Pavlovic, C. Barriga, M.C. Hermosin, *Appl. Clay Sci.* 18 (2001) 17.
- [15] D. Carriazo, C. Martin, V. Rives, A. Popescu, B. Cojocaru, I. Mandache, V.I. Parvulescu, *Micropor. Mesopor. Mater.* 95 (2006) 39.
- [16] D. Tichit, B. Coq, S. Cerneaux, R. Durand, *Catal. Today* 75 (2002) 197.
- [17] (a) C.A. Hamilton, S.D. Jackson, G.J. Kelly, *Appl. Catal. A: Gen.* 263 (2004) 63;  
(b) D. Tichit, B. Coq, *Catal. Technol.* 7 (2003) 206;  
(c) D. Tichit, M. Lhouty, A. Guida, B. Chiche, F. Figueras, A. Auroux, D. Bartalini, E. Garrone, *J. Catal.* 151 (1995) 50.
- [18] D. Tichit, M.J.M. Ortiz, D. Francová, C. Gérardin, B. Coq, R. Durand, F. Prinetto, G. Ghiotti, *Appl. Catal. A: Gen.* 318 (2007) 170.
- [19] (a) P. Kuśtrowski, D. Sulowska, L. Chmielarz, R. Dziembaj, *Appl. Catal. A: Gen.* 302 (2006) 317;  
(b) M.J. Climent, A. Corma, S. Iborra, J. Primo, *J. Catal.* 151 (1995) 60;  
(c) D. Tichit, C. Gérardin, R. Durand, B. Coq, *Top. Catal.* 39 (2006) 89.
- [20] R. Tessier, D. Tichit, F. Figueras, J. Kervenal, US 5,672,764 (1995).
- [21] F. Figueras, D. Tichit, M.B. Naciri, R. Ruiz, in: F.E. Herkes (Ed.), *Catalysis of Organic Reactions*, Marcel Dekker, New York, 1998, p. 37.
- [22] D. Tichit, M.N. Bennani, F. Figueras, R. Tessier, J. Kervenal, *Appl. Clay Sci.* 13 (1998) 401.
- [23] D. Tichit, D. Lutic, B. Coq, R. Durand, R. Teissier, *J. Catal.* 219 (2003) 167.
- [24] J. Sebastian, K.M. Jinka, R.V. Jasra, *J. Catal.* 244 (2006) 208.
- [25] J.S. Valente, F. Figueras, M. Gravelle, J. Lopez, J.-P. Besse, *J. Catal.* 189 (2000) 370.
- [26] S.K. Sharma, V.K. Srivastava, R.V. Jasra, *J. Mol. Catal. A: Chem.* 245 (2005) 200.
- [27] P. Kustrowski, D. Sulowska, L. Chmielarz, A. Rafalska-Lasocha, B. Dudek, R. Dziembaj, *Micropor. Mesopor. Mater.* 78 (2005) 11.
- [28] S.K. Sharma, P.K. Kushwaha, V.K. Srivastava, S.D. Bhatt, *Ind. Eng. Chem. Res.* 46 (2007) 4856.
- [29] L. Yang, Y. Aizhen, X. Qinhu, *Appl. Catal.* 67 (1991) 169.
- [30] M. Huang, S. Kaliaguine, A. Auroux, *Stud. Surf. Sci. Catal.* 97 (1995) 31.
- [31] M.F. Ciraolo, J.C. Hanson, C.P. Grey, *Micropor. Mesopor. Mater.* 49 (2001) 111.
- [32] R.T. Sanderson, *Chemical Bonds and Bond Energy*, Academic Press, New York, 1976, p. 218.
- [33] J.I. Di Cosimo, V.K. Díez, M. Xu, E. Iglesia, C.R. Apesteguía, *J. Catal.* 178 (1998) 499.
- [34] K.K. Rao, M. Gravelle, J.S. Valente, F. Figueras, *J. Catal.* 173 (1998) 115.
- [35] M.J. Climent, A. Corma, S. Iborra, A. Velty, *Green Chem.* 4 (2002) 474.
- [36] K. Ebitani, K. Motokura, K. Mori, T. Mizugaki, K. Kaneda, *J. Org. Chem.* 71 (2006) 5440.