

Mg/Al hydrotalcites: preparation, characterisation and ketonisation of acetic acid

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Received 28 October 1998; received in revised form 14 May 1999; accepted 14 May 1999

Abstract

Mg/Al hydrotalcites with different Mg:Al ratios were prepared and characterized by PXRD, FTIR, TG/DTA, basic sites and nitrogen adsorption–desorption methods. It is confirmed from PXRD that the materials have hydrotalcite structure. The basic sites of the samples were determined spectrophotometrically by irreversible adsorption of acids having different pK_a values which showed that the basic sites increases with increase in Mg:Al ratio. The specific surface area of all samples lies in the range 170–231 m^2/g . All the samples were predominantly mesoporous in nature and pore diameters lie in the range 40–70 Å. The sample with Mg:Al ratio of 4:1 showed highest specific surface area and conversion (> 86.5%) of acetic acid to acetone with high selectivity at 350°C. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrotalcite; Characterisation; Ketonisation; Acetic acid; Yield

1. Introduction

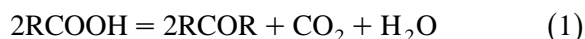
Anionic clays, particularly hydrotalcites, are class of layered materials of current interest. Hydrotalcites have brucite-like positively charged layer of magnesium and aluminium hydroxide octahedra sharing edges to form infinite sheets stacked on top of each other and are held together by hydrogen bonding. Due to isomorphous substitution of metal(III) ions, the positive charge thus generated on the brucite sheet is compensated by the anions present in the inter layer region. They are represented by the general formula $[M(II)_{1-x} M(III)_x(OH)_2]^{x+} [A_{x/n}^{n-}]_{x-}$, YH_2O , where M(II) and

M(III) are divalent and trivalent cations such as Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Al^{3+} , Fe^{3+} , Cr^{3+} , respectively, A^{n-} is the inter layer anion such as Cl^- , NO_3^- , CO_3^{2-} or any other macrocyclic multivalent anions, etc., and $x = 0.1–0.33$ [1,2]. Thermal decomposition of these materials at 450°C results in the formation of high surface area, basic mixed metal oxides due to the removal of surfacial and physisorbed water, and carbon dioxide molecules which are found to be promising catalyst for base catalyzed reactions. The activity and selectivity of these solids have been established for several reactions such as aldol condensation, olefin isomerisation, alkylation of ketones, etc.

Catalytic ketonisation by direct synthesis method is simple, economical and versatile. Oxides of thorium [3], cerium [4], manganese [5],

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zirconium [6], rare earth metals [7] as well as alkaline earth metals [8] and metal oxides supported on inorganic carriers such as alumina, silica or titania are found to be active catalyst for this reaction. The present work deals with a systematic study on Mg/Al hydrotalcite with different Mg:Al ratios for the vapour phase conversion of acetic acid to acetone which proceeds according to the general equation:



2. Experimental

2.1. Materials and methods

Hydrotalcites with various Mg:Al ratios were prepared by coprecipitation at low supersaturation method [9]. In this method, two solutions, A and B, were added at the same rate (50 ml/h) to a beaker containing 100 ml of deionised water while stirring. Solution A was prepared by mixing an equimolar solutions of Mg and Al metal nitrates (200 ml) in the desired molar ratios. Solution B was prepared by dissolving 14 g sodium hydroxide (0.35 mol) and 15.9 g sodium carbonate (0.15 mol) in 200 ml deionised water. The pH of the suspensions were around 10. The precipitates were aged at 65°C for 18 h in a thermostatic bath. The resulting product was filtered, washed thoroughly with deionised water until the filtrate showed no presence of NaOH and subsequently dried at 90°C for 24 h. Part of the samples were heated at 450°C for 18 h in a muffle furnace for further characterisation and catalytic activity study.

3. Characterisation

3.1. Chemical analysis

The bulk elemental analysis for magnesium and aluminium were done by chemical methods. A known weight of the sample was dissolved in 1:1 HCl. For aluminium estimation, a suitable

aliquot was taken, precipitated as hydroxide with 1:1 ammonia solution followed by filtration and dissolving the precipitate in 1:1 HCl and titrated by back titration method. The magnesium content in the filtrate was estimated by titration with EDTA using Eriochrome Black Tea indicator [10]. The sodium content in the calcined samples was determined by Flamephotometer.

3.2. Powder X-ray diffraction

The crystal structures of the calcined and uncalcined samples were examined by X-ray powder diffractometer and the patterns were recorded with Phillips model 1710 semiautomatic X-ray diffractometer with auto divergent slit and graphite monochromator using Cu K α radiation at a scanning speed of 2°/min, operated at 40 kV and 20 mA.

3.3. FTIR and thermal analysis study

FTIR spectra of the samples were recorded from 180 to 4000 cm $^{-1}$ in KBr phase with a Perkin-Elmer FTIR spectrophotometer. TG/DTA of the uncalcined samples were carried out in nitrogen atmosphere using a Perkin-Elmer, USA (Model DTA 1700/TG52/TADS 3600) at a heating rate of 15°/min in the temperature range 30–1000°C.

3.4. Textural properties

Specific surface area, pore volume, average pore diameter and pore size distribution were determined by nitrogen adsorption–desorption at liquid nitrogen temperature (–196°C) using a Quantasorb (Quantachrome, USA). Prior to adsorption–desorption measurement, the samples were equilibrated by degassing at 120°C at 10 $^{-4}$ Torr for 6 h.

3.5. Surface basicity

The surface basicity of the calcined samples were determined on the basis of the irreversible

adsorption of noninteracting acids, such as (acrylic acid, $pK_a = 4.2$) and (phenol $pK_a = 9.9$). Before basicity measurement, all catalysts were thoroughly degassed at 120°C under static air condition in a muffle furnace. The catalysts were then weighed (0.05 g) to stoppered bottles. To these bottles containing the catalysts, 10 ml of freshly prepared solution of phenol/acrylic acid in cyclohexane was pipetted out and were shaken for 2 h at 30°C keeping the mouth of the bottles closed. It was assumed that the interaction of the catalysts with atmospheric CO_2 and water was very negligible since the exposure of the samples to atmosphere was for a very short period (during weighing only). The concentration of the substrate in solution in equilibrium with the adsorbed substrate was determined spectrophotometrically [11]. Sorption experiments were developed at the wavelength of maximum adsorption (λ_{max} , nm) and in the concentration range of the adsorbate where the Beer–Lambert Law holds good. In each experiment, the time required to achieve equilibrium condition at constant temperature was checked and never found to be more than 2 h. The chemical interaction between adsorbate and catalyst surface was consistent with the Langmuir adsorption isotherm equation:

$$c/X = (1/bX_m) + c/X_m, \quad (2)$$

where c is the concentration of the substrate in solution, in equilibrium with the adsorbed substrate, b is a constant, X is the amount of adsorbed substrate per gram of catalyst and X_m is the monolayer coverage which correspond to the theoretical amount of the solute adsorbed by 1 g of solute if all sites are covered. This method, which makes use of organic acids of different pK_a values, provides both the total concentration of the basic sites and their relative strength. Similar method was adopted elsewhere [12].

3.6. Ketonisation of acetic acid

Catalytic ketonisation reaction was carried out in a fixed bed quartz reactor (10 mm, id) on

line with gas chromatograph. The reactor was placed inside a programmable tubular furnace (Stanton Red Croft, UK) containing 0.25 g of the catalyst. A nitrogen flow saturated with acetic acid vapour at room temperature was run through the catalyst. Prior to the catalytic test, each sample was pretreated under nitrogen flow at the lowest reaction temperature in the stream of reactant for 2 h. The products were analyzed by on line gas chromatograph (CIC, India) operated on FID mode and using a porapak Q column. The authenticity of the products were verified by comparing the retention time with the standard sample.

4. Results and discussion

The XRD pattern of the 90°C dried samples (Fig. 1) show sharp and symmetric peaks which gives clear indication that the samples are well crystallised and the peaks corresponding to (003), (006), (110) and (113) planes are characteristic of clay mineral (hydrotalcite) having layered structure [13]. In the case of calcined samples, the (003) and (006) reflections, which give the basal spacing $d(003)$, practically disappear indicating that the hydrotalcite structure is mainly destroyed after calcination at 450°C and there is disorder in the stacking in the layers. In all the uncalcined samples, the intensity of the corresponding peaks decreases as the Mg:Al ratio increases.

The IR spectrum of the uncalcined hydrotalcite samples shown in Fig. 2 possess an intense broadband between 4000 and 2700 cm^{-1} which may be represented as a superimposition of deformational vibrations of physically adsorbed water [14], vibrations of structural OH^- groups [15], characteristic valent vibrations of $\text{HO}\dots\text{OH}$ and/or $\text{CO}_3^{2-}\text{-OH}^-$ in hydrotalcite [16] and of characteristic stretching vibration of the $\text{Mg}^{2+}\text{-OH}^-$ bond in Mg, Al-hydroxycarbonate [14]. The band at around 1632 cm^{-1} (bending vibration of δHOH) may be assigned to the adsorbed interlayer water. An intense

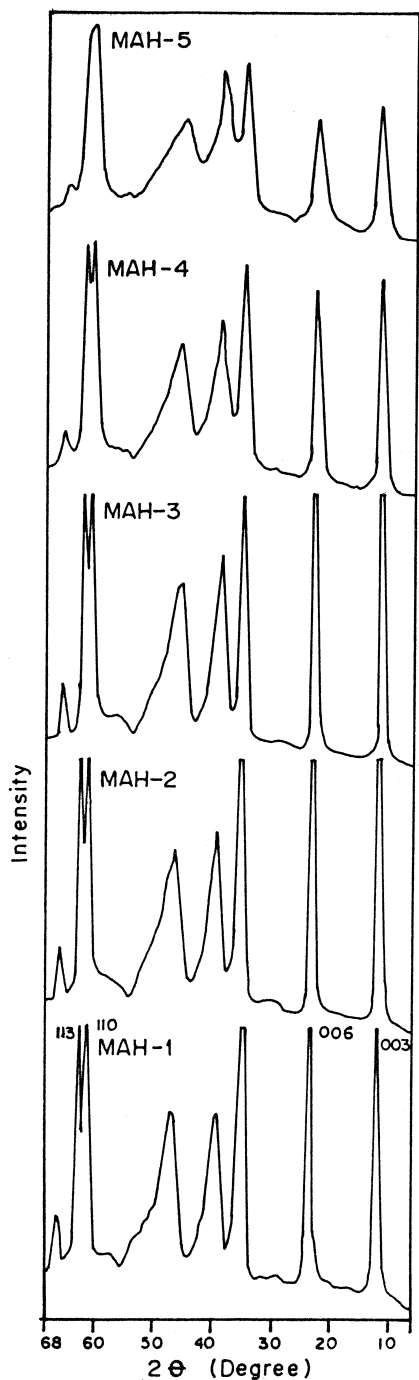


Fig. 1. XRD patterns of 90°C dried Mg/Al hydrotalcite with different Mg:Al molar ratios.

absorption band at 1383 cm^{-1} is attributed to the CO_3^{2-} absorption and the impurities of NO_3^- which may be the result from the synthesis

solution [17,18]. The broadband at around 663 cm^{-1} most probably is a superposition of the characteristic bonds of boehmite or hydrotalcite in this frequency interval [19]. The doublet at around 791 and 663 cm^{-1} coincides by position and intensity ratio with the corresponding characteristic vibrations of hydrotalcite [16]. Upon calcination, there is a significant decrease in the intensity of water and carbonate characteristic peaks due to the removal of water and CO_2 vapours.

The DTA peaks obtained from the thermal analysis studies of the samples are presented in Fig. 3 which exhibit a two-step weight loss process. The first step below 250°C is attributed to loosely bound water in the interlayer space and the second one below 425°C is due to the simultaneous dehydroxylation and decarbonation of the lattice OH^- , strongly bound water and CO_3^{2-} groups.

The specific surface area, average pore diameter and pore volume are presented in Table 1.

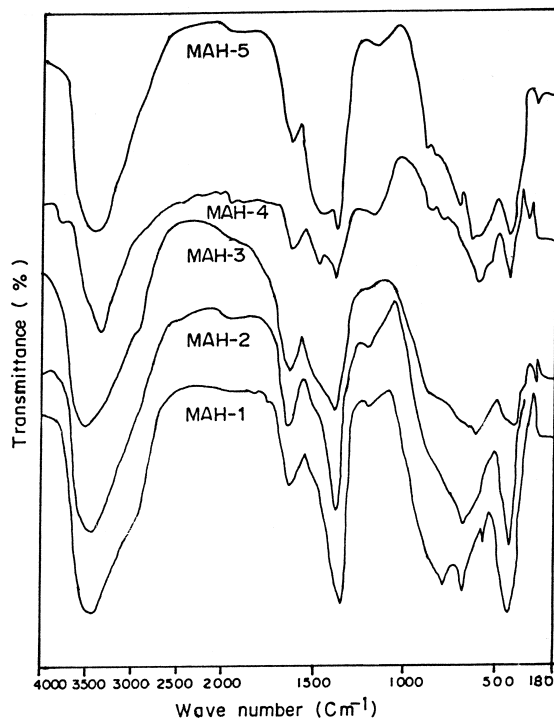


Fig. 2. IR spectrum of 90°C dried Mg/Al hydrotalcite with different Mg:Al molar ratios.

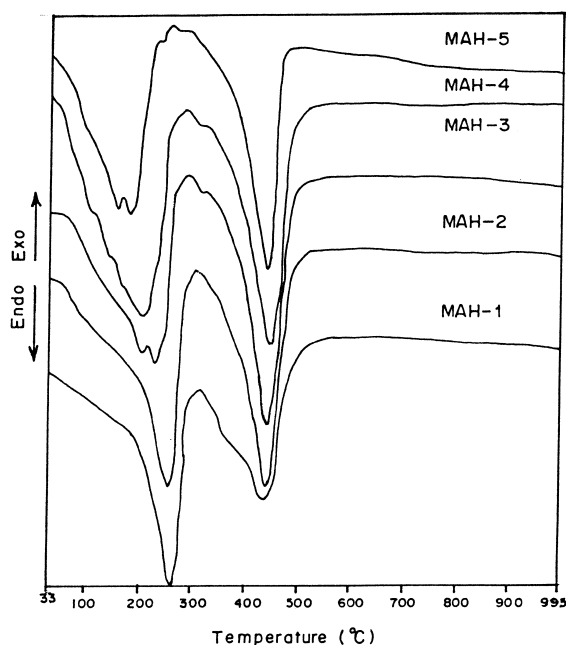


Fig. 3. DTA curves of Mg/Al hydrotalcite with different Mg:Al molar ratios.

The specific surface area of the samples increases with the increase in Mg:Al ratio up to 4:1 and thereafter decreases. The sample with Mg:Al ratio 4:1 shows highest surface area of $231 \text{ m}^2/\text{g}$. The adsorption–desorption isotherm of the materials, which is shown in Fig. 4, are nearly of type-IV in BDDT classification [20]. In the case of all the samples, the hysteresis loop starts at a high relative pressure which supports the mesoporous nature of the samples. From the nature of the loop, it can be concluded that the pores are of uniform shape and size.

Assuming the pores to be cylindrical, the average pore diameter is calculated by using the formula $d = 4V_p/S_p$ where d is the average pore diameter, V_p is the pore volume and S_p is the specific internal surface area of the pores. The average pore diameter is found to be in the range 40–70 Å. This is also supported by the mesopore size distribution curve calculated by BJH equation [21] which is shown in Fig. 5.

Since adsorption depends upon the pK_a values of the organic acids, the values for phenol adsorption measure strong basic sites, whereas acrylic acid measures the total basicity of the sample. For a particular solid, the weak basic sites can be measured from the difference of values of acrylic acid and phenol adsorption. It is observed from Table 1 that the basic sites increases with the increase in Mg:Al ratio and all the samples have very few number of strong basic sites.

Ketonisation of acetic acid over Mg/Al hydrotalcites with different Mg:Al ratios are shown in Fig. 6. As the material is highly basic in nature as evident from the basic site data, it is expected that the products in the ketonisation of acetic acid are acetone, carbon dioxide and water. From the reaction profile, it is evident that the conversion starts at 300°C in case of samples with Mg:Al ratios of 2:1 to 4:1 and in case of samples with Mg:Al ratio 5:1 and 7:1 it starts at a higher temperature. The maximum activity for conversion of acetic acid is shown by sample prepared with Mg:Al ratio of 4:1. In this case, a maximum conversion of $> 86.5\%$ was

Table 1
Textural properties of Mg/Al hydrotalcites prepared with different Mg:Al ratios

| Sample code | Mg:Al sample molar ratio | Mg/Al atomic ratio | S_{BET} (m^2/g) | Average pore diameter (Å) | Pore volume (cm^3/g) | Basic sites | | Na (%) |
|-------------|--------------------------|--------------------|--|---------------------------|--|-----------------------|-----------------|--------|
| | | | | | | Acrylic acid (mmol/g) | Phenol (mmol/g) | |
| MAH-1 | 2:1 | 1.84 | 219.44 | 58.06 | 0.29 | 7.54 | 0.16 | 0.011 |
| MAH-2 | 3:1 | 2.80 | 196.36 | 64.28 | 0.26 | 8.34 | 0.24 | 0.008 |
| MAH-3 | 4:1 | 3.73 | 230.93 | 50.50 | 0.21 | 8.48 | 0.36 | 0.004 |
| MAH-4 | 5:1 | 4.68 | 192.72 | 42.64 | 0.23 | 8.69 | 0.41 | 0.005 |
| MAH-5 | 7:1 | 6.42 | 186.02 | 70.36 | 0.34 | 8.87 | 0.39 | 0.009 |

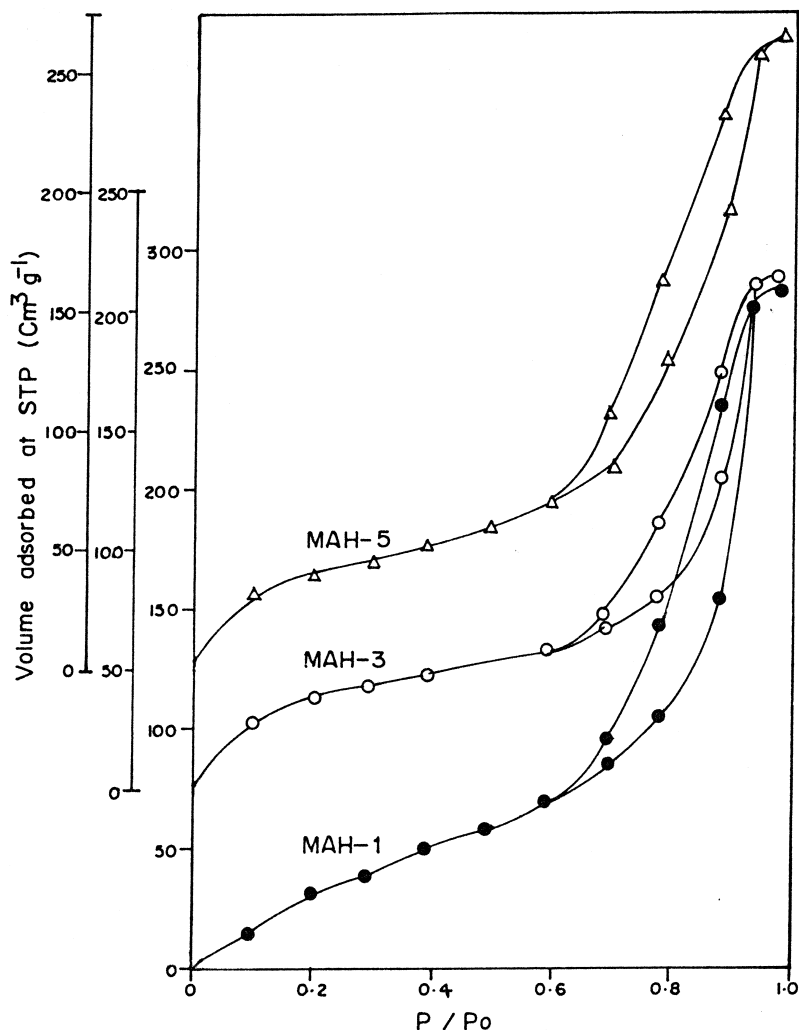


Fig. 4. Nitrogen adsorption–desorption isotherm of Mg/Al hydrotalcite; numbers refer to samples (cf. Table 1).

achieved at a temperature of 350°C and thereafter the conversion remains almost unchanged as the temperature is increased even to 400°C. Similar results have also been reported by others for hydrotalcites with Mg:Al ratio of 4:1 for various chemical reactions [22,23]. Parida and Mishra [24] have also achieved similar range of conversion in case of metal promoted zirconia in the temperature range 350–425°C using 0.5 g of sample under identical conditions. By varying different metal oxides such as MgO, CdO, CoO, Fe₂O₃, La₂O₃, CeO₂, MnO₂ on silica support, Glinski et al. [25] have observed that

the acetone yield reached better than 50% at 375°C. The higher activity of sample prepared with Mg:Al ratio of 4:1 could be due to its high specific surface area, comparatively small pore diameter and pore volume compared to other samples. Furthermore, a synergetic interaction between the metal oxides is obtained upon calcination of the precursor with high surface area and porosity which is absent in case of physically mixed oxides. Yekerson [8] and Yekerson et al. [26] have investigated some oxidic systems in detail and proposed two pathways through which acetic acid interact with the solid

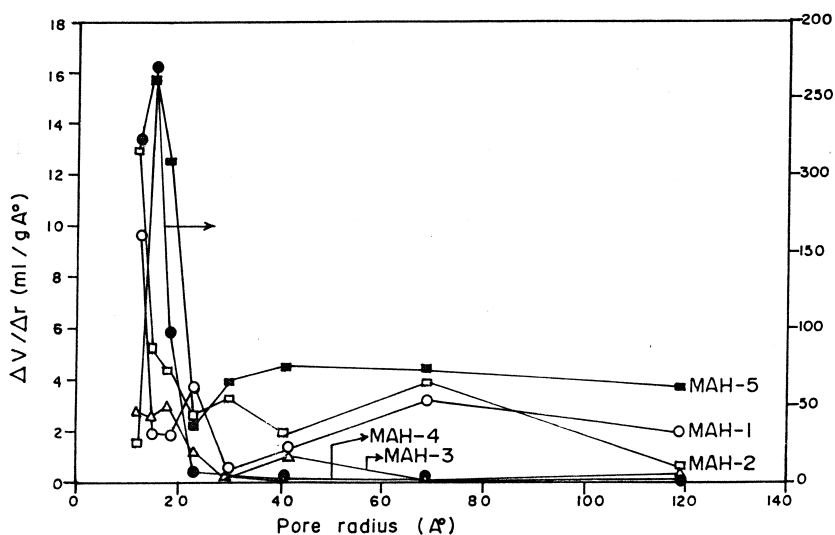


Fig. 5. Distribution of pore as a function of pore radius; numbers refer to samples (cf. Table 1).

to give acetone. These were (i) the formation of bulk acetates and their decomposition to acetone and (ii) surface interaction. The former path is generally followed by oxides of low lattice energy whereas the latter occurs preferentially with solids of high lattice energy. Mg/Al hydrotalcites being a compound of high lattice energy thus might be allowing surface interaction. It is seen from Fig. 7 that with the linear increase in

gas hourly space velocity (GHSV), a significant drop in acetone yield is observed in the temperature range 300–400°C and also a shift in the temperature of maximum conversion to higher values. This effect may be attributed to the variation in proportionate exposure of active sites to reactant concentration. A slight decrease in the activity is observed in time-on-stream

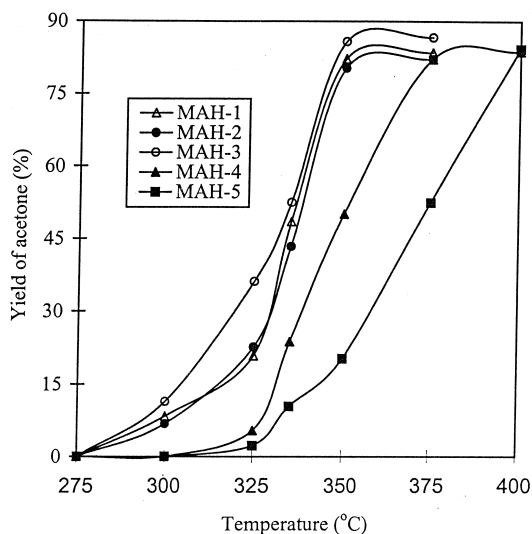


Fig. 6. Effect of Mg: Al ratio on the ketonisation of acetic acid. GHSV = 15000.

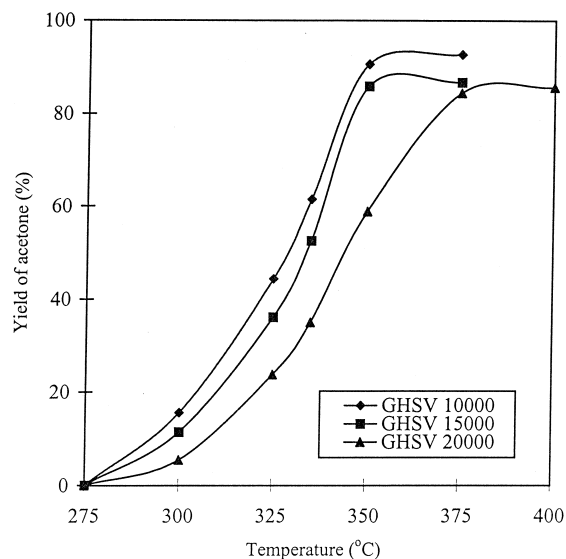


Fig. 7. Catalytic activity of MAH-3 on ketonisation of acetic acid at various GHSV.

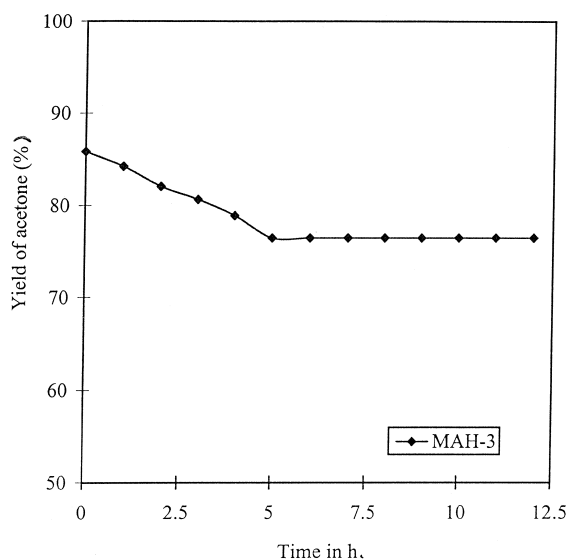


Fig. 8. Yield of acetone in time-on stream experiment over MAH-3 at 350°C, GHSV = 15000.

profile (Fig. 8) during the first 4 h of reaction at 350°C, and thereafter it remains almost constant.

5. Conclusions

Mg/Al hydrotalcite could find application in the ketonisation of acetic acid as it has appreciable number of basic sites, high thermal resistance and high specific surface area. The sample with Mg:Al ratio of 4:1 showed highest conversion (> 86.5%) of acetic acid with high selectivity at 350°C. Mg to Al combination in the ratio of 4:1 is most ideal for controlling electrostatic interaction between the layers so as to give highest surface area to the material. Being a high energy solid, prefers surface interaction with the acid for ketonisation.

Acknowledgements

The authors are very much thankful to Prof. H.S. Ray, Director, RRL, Bhubaneswar, for his

permission to publish this paper, and Dr. S.B. Rao, Head, IC Division, for his constant encouragement throughout the work.

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