

# Friedel-Crafts benzylation of benzene using Zn and Cd ions exchanged clay composites

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Received 2 June 2004; accepted 11 November 2004

## Abstract

Metal ion-exchanged clay composites such as M<sup>II</sup>-Mont and M<sup>II</sup>-Mont (AT) where M = Zn and Cd, Mont = montmorillonite clay of the types Mont<sub>1</sub> (SWy-2) and Mont<sub>2</sub> (Neelkanth), and AT = acid treated have been synthesized, characterized and evaluated as catalysts for Friedel-Crafts reaction particularly for benzylation of benzene. XRD study reveals that, in general, the basal spacing ( $d_{001}$ ) increases as the interlayer cations of Na-Mont or H<sup>+</sup>-Mont are exchanged with Zn<sup>2+</sup> or Cd<sup>2+</sup> ions and interlamellar spacings are maintained in the range 3.9–5.3 and 4.3–6.0 Å, respectively, at room temperature. The basal spacing ( $d_{001}$ ) of Mont<sub>1</sub> supported composites are higher than Mont<sub>2</sub> and therefore substantiate the advantage of the former over the latter in preparing metal ion-exchanged clay composites useful as solid acid catalysts. During the initial benzylation reactions, Cd<sup>2+</sup>-exchanged composites, in general, show higher activity but in the long run Zn<sup>2+</sup>-exchanged clays exhibit higher catalytic activities. In general, acid treated metal ion-exchanged clay composites exhibit higher catalytic activity than non-acid treated ones because the former show higher surface area as well as higher acid sites.

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**Keywords:** Montmorillonite clay; Solid acid catalysts; Friedel-Crafts reaction; Benzylation of benzene; Interlamellar spacings

## 1. Introduction

Different types of modified supported inorganic reagents are rapidly emerging as new and environment friendly materials [1]. Attempts are being made to replace highly corrosive HF in olefin alkylation, anhydrous AlCl<sub>3</sub> in Friedel-Crafts alkylation, etc. by such supported solid acid catalysts. Replacement of the exchangeable interlayer Na<sup>+</sup> ions of montmorillonite (Mont) clay by high charge density cations such as Al<sup>3+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup> leads to clay layers of high acidity and are described as broad spectrum catalysts for organic synthesis [1,2]. Such clays at high temperature reduce to Lewis acidity through the loss of interlayer water. It, therefore, appears that suitable supported metal ions on Mont may play key role as solid acid catalysts in reactions like Friedel-Crafts alkyla-

tions [3–6]. Treatment of clays with acid has been reported to replace exchangeable cations with H<sup>+</sup> ions and leaching Al<sup>3+</sup> out of both tetrahedral and octahedral sites but leaving the SiO<sub>4</sub> group largely intact [7]. Such acid treated clays are therefore partially delaminated and exhibit higher surface area, pore volume and pore diameter but lower CEC values than the parent clays [3,8–10]. The exchangeable cations in these materials play a key role in controlling surface acidity and catalytic activity. Presence of protons and coordinatively unsaturated cationic centers on the surface and interlamellar spacing of the clay impart Brønsted and Lewis acidities to it.

Replacement of environmentally unacceptable anhydrous AlCl<sub>3</sub>, an established catalyst for Friedel-Crafts alkylation, by supported AlCl<sub>3</sub> on Mont K10 (an acid treated Mont) has been claimed to be an efficient catalyst [11]. Another such example is ‘Clayzic’ which exhibits both Brønsted and Lewis surface acidities [3,12], which is prepared by deposition of ZnCl<sub>2</sub> on Mont K10. Good conversion are also achieved

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in Friedel-Crafts alkylation by using transition metal ion-exchanged Mont K10 [13,14].

The present work reports the preparation of metal ion-exchanged clay composites like  $M^{II}$ -Mont and  $M^{II}$ -Mont (AT) (where  $M = \text{Zn, Cd}$ ; AT = acid treated) and their solid acid catalytic activities towards Friedel-Crafts benzylation of benzene. These metal ions exchanged clay composites have been characterized by X-ray diffraction analysis, surface area and acid sites determination.

## 2. Experimental

### 2.1. Materials and methods

Two Mont clays were chosen for studies: (1) bentonite (SWy-2) from Crook County Wyoming USA (Mont<sub>1</sub> hereafter) and (2) bentonite from Neelkanth Sodaclays and Pulverizers, Jodhpur, India (Mont<sub>2</sub> hereafter). Clays contained silica sand, iron oxide, etc. as impurities and were purified by the sedimentation method [15] to collect the  $<2 \mu\text{m}$  fraction. The oxide compositions of the Mont<sub>1</sub> and Mont<sub>2</sub> determined by weight chemical and flame photometric methods were  $\text{SiO}_2$ : 58.12 and 49.42;  $\text{Al}_2\text{O}_3$ : 18.93 and 20.02;  $\text{Fe}_2\text{O}_3$ : 4.63 and 7.49;  $\text{MgO}$ : 2.52 and 2.82;  $\text{CaO}$ : 1.12 and 0.69; LOI: 13.54 and 17.51; others ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{TiO}_2$ ) 1.14 and 2.05 wt.%, respectively.

The clays were converted to the homoionic Na-exchanged form Na-Mont by stirring in 2 M NaCl solution for about 78 h, which was washed and finally dialyzed against distilled water until conductivity of the dialysate approached that of distilled water. The cation exchange capacities (CEC) of Mont<sub>1</sub> and Mont<sub>2</sub> clay as determined [16] were found to be 80 and 114 mequiv./100 g of clay, respectively.

### 2.2. Preparation of $M^{II}$ -Mont

A volume of 100 ml of 1% slurry of Na-Mont in aqueous medium was treated with equal volume of 2 M metal chloride ( $\text{MCl}_2$ ) solution (where  $M = \text{Zn, Cd}$ ) and stirred for a period of 12 h and then set aside for settling. The supernatant salt solution was removed and again 100 ml of 2 M metal chloride solution was added. Stirring and removal of supernatant solution was repeated and then distilled water was added, stirred, settled and decanted off. The large excess of salt was removed by this process. When the clay stopped settling, the remaining salt was removed by dialysis of the product against distilled water till the conductivity of the dialysate approached that of distilled water and showed negative test for  $\text{Cl}^-$  with silver nitrate. The metal cation-exchanged Mont ( $M^{II}$ -Mont) composites thus obtained were dried at  $50 \pm 5^\circ\text{C}$  in air oven to obtain the solid products.

### 2.3. Acid treatment of Mont

An amount of 3 g of dry  $<2 \mu\text{m}$  fraction clay particles was treated with 100 ml of 0.7 M HCl and the slurry was refluxed

for 4 h. After cooling, the slurry was filtered under suction, washed with distilled water and finally dialysed against distilled water till the conductivity of the dialysate approached that of distilled water and showed negative test for  $\text{Cl}^-$  with silver nitrate. The mass was then dried at  $50 \pm 5^\circ\text{C}$  in air oven to obtain the solid product. The CEC of the acid treated clays  $\text{H}^+$ -Mont were found to be 35 and 70 mequiv./100 g clay for Mont<sub>1</sub> and Mont<sub>2</sub> clays, respectively.

### 2.4. Synthesis of $M^{II}$ -Mont (AT)

A volume of 100 ml of 1% slurry of  $\text{H}^+$ -Mont in aqueous medium was treated with equal volume of 2 M metal chloride ( $\text{MCl}_2$ ) solution (where  $M = \text{Zn, Cd}$ ) and stirred for a period of 12 h and then set aside for settling. The supernatant salt solution was removed and again added 100 ml of 2 M metal chloride solution. Stirring and removal of supernatant solution was repeated and then distilled water was added, stirred, settled and decanted off. The large excess of salt was removed by this process. When the clay stopped settling, the remaining salt was removed by subjecting the slurry to dialysis against distilled water till the conductivity of the dialysate approached that of distilled water and showed negative test for  $\text{Cl}^-$  ion with silver nitrate. The metal ion-exchanged acid treated Mont ( $M^{II}$ -Mont (AT)) so produced was then dried at  $50 \pm 5^\circ\text{C}$  in an air oven to obtain the solid products.

### 2.5. Basal spacing ( $d_{001}$ ) determination by XRD technique

Thin layered (oriented) samples were prepared on glass slides by standard technique [17,18] for basal spacing ( $d_{001}$ ) determination by XRD. Diffraction patterns were taken in the range  $2\theta = 2-60^\circ$  at a rate of  $6^\circ/\text{min}$  (X-ray diffractometer JEOL, JDX-11p 3A, Japan).

### 2.6. Acid sites determination

The catalysts were degassed at  $150^\circ\text{C}$  under flowing nitrogen for 2 h. Ammonia gas was then purged at  $100^\circ\text{C}$  for 2 h. The amount of acid sites were determined from the desorption of chemisorbed ammonia by thermogravimetric analysis (TA instruments, Model STD 2960 simultaneous DTA-TGA) in the temperature range  $150-650^\circ\text{C}$ .

### 2.7. Surface area measurement

Surface area of the clay composites were determined by  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$  and application of the BET equation. Prior to adsorption, clay samples were degassed at  $150^\circ\text{C}$  for about 2 h. The adsorption and desorption isotherm were recorded on a Smart Sorb 91 Surface Area Analyser.

### 2.8. Procedure for benzylation of benzene

The  $M^{II}$ -Mont,  $\text{H}^+$ -Mont and  $M^{II}$ -Mont (AT) composites for both the clays Mont<sub>1</sub> and Mont<sub>2</sub> were used as Friedel-

Crafts catalysts, particularly for benzylation of benzene. Catalysts were activated under dry air at 150 °C for 3 h. A typical experiment may be described as mixing 8 ml of benzene and 0.24 ml of benzyl chloride in a round bottom flask and stirred at room temperature with the catalyst (containing 0.105 mmol cation). The product, diphenylmethane, was collected at different time intervals and analysed by GC (Chemito GC, Model 8510, FID).

### 3. Results and discussion

#### 3.1. X-ray diffraction studies

The XRD patterns along with basal spacing ( $d_{001}$ ) of Na–Mont<sub>1</sub>, Na–Mont<sub>2</sub>, Zn<sup>II</sup>–Mont<sub>1</sub>, Zn<sup>II</sup>–Mont<sub>2</sub>, Cd<sup>II</sup>–Mont<sub>1</sub> and Cd<sup>II</sup>–Mont<sub>2</sub> are shown in Fig. 1. The basal spacing ( $d_{001}$ ) of Na–Mont<sub>1</sub> (12.4 Å) shows an increase when the interlayer cations are exchanged with Zn<sup>2+</sup> and Cd<sup>2+</sup> ions and the values are 14.6 and 14.9 Å, respectively. Similarly, basal spacing ( $d_{001}$ ) values of Zn<sup>II</sup>–Mont<sub>2</sub> and Cd<sup>II</sup>–Mont<sub>2</sub> are 13.7 and 13.5 Å, respectively, as compared to that of Na–Mont<sub>2</sub> (12.5 Å). Thus, it reveals that Zn<sup>2+</sup>/Cd<sup>2+</sup> exchanged clays maintain interlamellar spacing in the range 3.9–5.3 Å at room temperature and in general Mont<sub>1</sub> supported composites show higher basal spacing ( $d_{001}$ ) as compared to Mont<sub>2</sub> supported composites which substantiate the advantage of Mont<sub>1</sub> over Mont<sub>2</sub> as catalyst support.

The XRD patterns of H<sup>+</sup>–Mont<sub>1</sub>, H<sup>+</sup>–Mont<sub>2</sub>, Zn<sup>II</sup>–Mont<sub>1</sub> (AT), Zn<sup>II</sup>–Mont<sub>2</sub> (AT), and Cd<sup>II</sup>–Mont<sub>1</sub> (AT) and Cd<sup>II</sup>–Mont<sub>2</sub> (AT) along with their basal spacing ( $d_{001}$ ) are

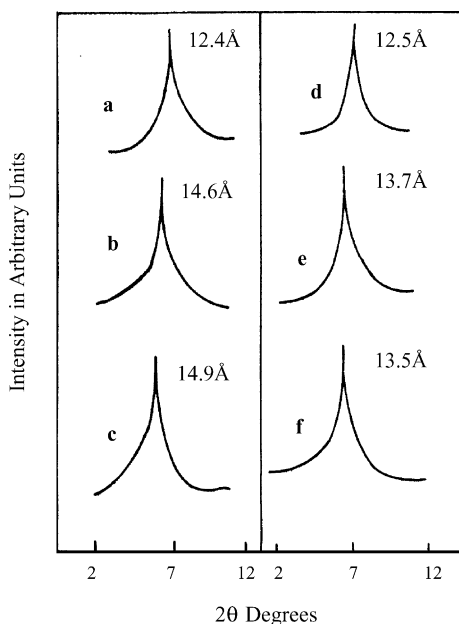


Fig. 1. XRD patterns and basal spacing ( $d_{001}$ ) of Na–Mont<sub>1</sub> (a), Zn<sup>II</sup>–Mont<sub>1</sub> (b), Cd<sup>II</sup>–Mont<sub>1</sub> (c), Na–Mont<sub>2</sub> (d), Zn<sup>II</sup>–Mont<sub>2</sub> (e) and Cd<sup>II</sup>–Mont<sub>2</sub> (f).

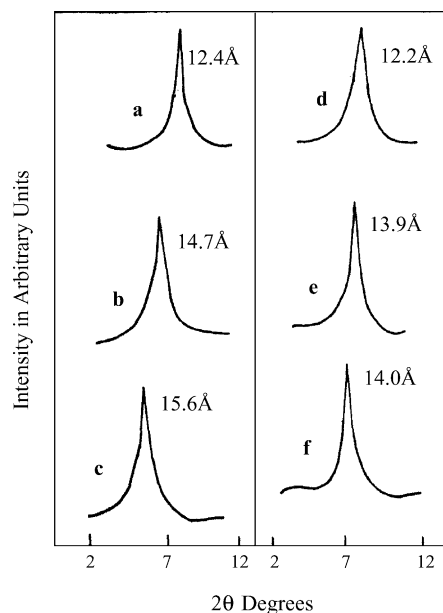


Fig. 2. XRD patterns and basal spacing ( $d_{001}$ ) of H<sup>+</sup>–Mont<sub>1</sub> (a), Zn<sup>II</sup>–Mont<sub>1</sub> (AT) (b), Cd<sup>II</sup>–Mont<sub>1</sub> (AT) (c), H<sup>+</sup>–Mont<sub>2</sub> (d), Zn<sup>II</sup>–Mont<sub>2</sub> (AT) (e) and Cd<sup>II</sup>–Mont<sub>2</sub> (AT) (f).

shown in Fig. 2. The basal spacing ( $d_{001}$ ) of H<sup>+</sup>–Mont<sub>1</sub> and H<sup>+</sup>–Mont<sub>2</sub> are 12.4 and 12.2 Å, respectively, implying that the laminar structures of the clays are retained to a significant degree even after acid treatment. Fig. 2 shows that the basal spacing ( $d_{001}$ ) of Zn<sup>2+</sup>-exchanged acid treated Mont clays are 14.7 and 13.9 Å for Zn<sup>II</sup>–Mont<sub>1</sub> (AT) and Zn<sup>II</sup>–Mont<sub>2</sub> (AT), respectively, while the basal spacing ( $d_{001}$ ) of Cd<sup>2+</sup>-exchanged acid treated Mont clays, i.e. Cd<sup>II</sup>–Mont<sub>1</sub> (AT) and Cd<sup>II</sup>–Mont<sub>2</sub> (AT) show higher values at 15.6 and 14.0 Å, respectively. Thus it reveals that the acid treated metal ion-exchanged clay composites maintain the layered structures having interlayer spacing of about 4.3–6.0 Å at room temperature. Such composites are found to be stable up to about 200 °C. These layered composites are likely to act as size/shape selective catalysts.

#### 3.2. Acid site and surface area data

The amount of acid sites (Brønsted and Lewis) were determined from the desorption of ammonia in the temperature range 150–650 °C of ammonia treated highly active Zn<sup>2+</sup> containing composites are shown in Table 1. It reveals from Table 1 that the amount of acid sites as well as surface

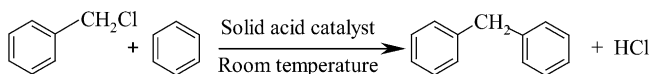
Table 1  
Acid sites and surface area of different Zn<sup>II</sup> containing catalysts

Catalyst	Amount of acid sites (mmol/g)	Surface area (m <sup>2</sup> /g)
Zn <sup>II</sup> –Mont <sub>1</sub>	1.299	72.89
Zn <sup>II</sup> –Mont <sub>1</sub> (AT)	1.612	93.91
Zn <sup>II</sup> –Mont <sub>2</sub>	1.176	40.55
Zn <sup>II</sup> –Mont <sub>2</sub> (AT)	1.415	54.26

area of acid treated metal ion-exchanged clay composites are higher than non-acid treated ones.

### 3.3. Benzylation of benzene with benzyl chloride

Benylation of benzene to produce diphenylmethane (Eq. (1)) in presence of different solid acid catalysts like  $\text{Zn}^{\text{II}}\text{-Mont}_1$ ,  $\text{Zn}^{\text{II}}\text{-Mont}_2$ ,  $\text{Cd}^{\text{II}}\text{-Mont}_1$ ,  $\text{Cd}^{\text{II}}\text{-Mont}_2$ ,  $\text{H}^+\text{-Mont}_1$ ,  $\text{H}^+\text{-Mont}_2$ ,  $\text{Zn}^{\text{II}}\text{-Mont}_1$  (AT),  $\text{Zn}^{\text{II}}\text{-Mont}_2$  (AT),  $\text{Cd}^{\text{II}}\text{-Mont}_1$  (AT) and  $\text{Cd}^{\text{II}}\text{-Mont}_2$  (AT) at room temperature are studied in details. The major product, diphenylmethane,



Benzyl chloride    Benzene                                  Diphenylmethane    (1)

is collected at different time intervals and analyzed by gas liquid chromatography. Different yield percentages of diphenylmethane from benzylation of benzene against time in presence of different metal ion-exchanged clay catalysts at room temperature are shown in Fig. 3.  $\text{Zn}^{\text{II}}\text{-Mont}_1$  and  $\text{Cd}^{\text{II}}\text{-Mont}_1$  show initially 0.3 and 7.2% yields of diphenylmethane, respectively, up to a reaction period of 4 h, which enhance to 5.1 and 12.3%, respectively, during the period of 10 h, but on increasing the reaction time (24 h) a reverse trend of yields, i.e. 63.5 and 28.6%, respectively, are observed. On further increasing the reaction time up to 48 h, the composites  $\text{Zn}^{\text{II}}\text{-Mont}_1$  and  $\text{Cd}^{\text{II}}\text{-Mont}_1$  show the corresponding yields 99.8 and 94.3% and finally within 72 h of reaction time both the catalysts produce about 99.9% of diphenylmethane. In a similar manner,  $\text{Zn}^{\text{II}}\text{-Mont}_2$  and  $\text{Cd}^{\text{II}}\text{-Mont}_2$  show initially 0.2 and 1.0% conversion to diphenylmethane, respectively,

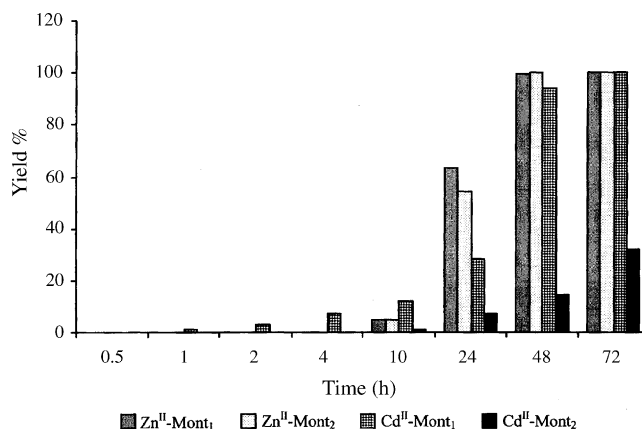


Fig. 3. The percentage yield of diphenylmethane in benzylation of benzene at room temperature against reaction time in presence of different metal ion-exchanged Mont catalysts.

in a reaction period of 4 h while during 10 h of reaction time, a reverse trend of yields, i.e. 4.9 and 2.4% are observed. On further increasing the reaction periods up to 24, 48 and 72 h the corresponding yields obtained are 54.6 and 7.4, 99.9 and 14.4, and 99.9 and 31.7%.

The conversion to diphenylmethane in presence of different acid treated and metal ion-exchanged clay catalysts at room temperature against time of reaction are shown in Fig. 4. The yields against  $\text{H}^+\text{-Mont}_1$ ,  $\text{Zn}^{\text{II}}\text{-Mont}_1$  (AT) and  $\text{Cd}^{\text{II}}\text{-Mont}_1$  (AT) catalysts are 1.2, 11.9 and 22.1%, respectively, within a period of 4 h, while in 10 h reaction time, a reverse trend between  $\text{Zn}^{\text{II}}\text{-Mont}_1$  (AT) and  $\text{Cd}^{\text{II}}\text{-Mont}_1$  (AT) is observed and the corresponding conversions are 5.3, 92.9 and 32.8% which enhance to 31.1, 99.9 and 46.7%,

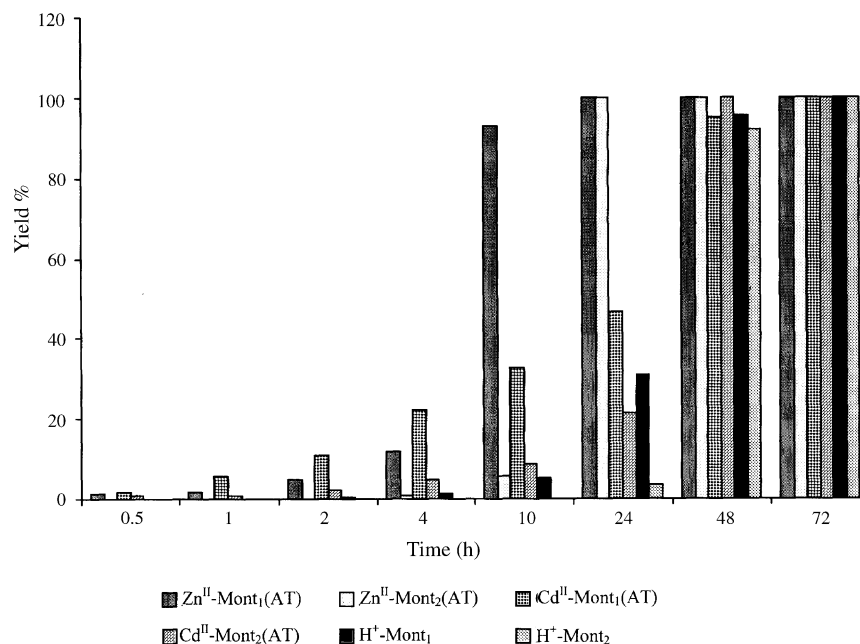


Fig. 4. The percentage yield of diphenylmethane in benzylation of benzene at room temperature against reaction time in presence of different acid treated metal ion-exchanged Mont catalysts.

respectively, during 24 h. During 48 h. reaction period, the corresponding conversions are 95.4, 99.9 and 94.9% and finally in 72 h, the yields of diphenylmethane are almost 100% irrespective of any catalysts. Similarly the yields of diphenylmethane (Fig. 4) against  $H^+$ -Mont<sub>2</sub>,  $Zn^{II}$ -Mont<sub>2</sub> (AT), and  $Cd^{II}$ -Mont<sub>2</sub> (AT) catalysts are 0, 0.7 and 4.9%, respectively, within a period of 4 h, while in 10 h the corresponding yields are 0, 5.7 and 8.9%. However, during 24 h reaction time the corresponding yields of diphenylmethane enhance to 3.3, 99.8 and 21.3% indicating a reverse trend of catalytic activity between  $Zn^{II}$ -Mont<sub>2</sub> (AT) and  $Cd^{II}$ -Mont<sub>2</sub> (AT) similar to that observed earlier. During 48 h reaction time, the corresponding yields are 92.3, 99.9 and 99.9 and finally, almost 100% conversions are found in 72 h. The catalysts are reusable. After catalytic experiments, the recovered catalysts after activation are found to show almost the same catalytic activities.

It is observed from the above that  $Cd^{2+}$ -exchanged clay composites exhibit higher initial activity than  $Zn^{2+}$ -exchanged composites but during the later period of the reaction  $Zn^{2+}$ -exchanged clay composites proved themselves to be better catalysts. The higher initial catalytic activity of  $Cd^{2+}$ -composites over  $Zn^{2+}$ -composites may be due to higher polarizing power and ease of formation of hexacoordinated sphere [19] of  $Cd^{2+}$  over  $Zn^{2+}$  but a reverse trend of catalytic activity of the composites is observed in the later part of the reaction. This trend is assumed to be due to stronger  $\pi$ -interaction between the organic moieties of the products and the metal orbitals of  $Cd^{2+}$ -composites over  $Zn^{2+}$  containing ones [20]. It is also revealed that Mont<sub>1</sub> clay is a better support than Mont<sub>2</sub> in preparing metal ion–clay composites in respect of their catalytic activity for benzylation of benzene. The acid treated metal ion-exchanged clay composites exhibit higher catalytic activity than non-acid treated ones because the former shows higher surface area as well as acid sites (Table 1).

### Acknowledgements

The authors are thankful to the Director, Regional Research Laboratory (CSIR), Jorhat, India, for his kind per-

mission to publish the work. The authors thank Head, Material Science Division, RRL, Jorhat, for his keen interest and support. One of the authors (OSA) is grateful to University Grants Commission, New Delhi for providing a Teacher Fellowship. The authors are also grateful to Council of Scientific and Industrial Research (CSIR), New Delhi, for granting a fund through a Net Work Project (No. CMM0005).

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