



# ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Montmorillonite composite: efficient solid acid catalyst for benzylation of benzene

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## Abstract

A newer type of metal salt–metal ion exchanged Montmorillonite (Mont), MCl<sub>2</sub>-M<sup>n+</sup>-Mont (M = Ni, Cu, Zn; n = 2) have been prepared and evaluated as solid acid catalysts for Friedel–Crafts reactions particularly for benzylation of benzene. The activity of such composites depends upon the amount of loading of metal salts on the metal ion exchanged-Mont support and 1.5 mmol loading per mole of the support shows the highest activity. Activation temperature of the composites also plays an important role and 150 ± 10 °C is the optimum region. ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont (1.5 mmol, 0.926 g) and Zn<sup>2+</sup>-Mont (1.5 mmol, 3.33 g) composites show about 97% conversion during 24 h of reaction time and therefore, the former composite shows an advantage over the latter in respect of total amount of catalyst weight to be used. The composites show both Bronsted and Lewis acidities which were determined by thermal desorption and differential scanning calorimetric (DSC) techniques. The composites were also characterized by thermal analysis and X-ray diffraction (XRD) measurements.

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**Keywords:** Activation temperature; Thermal desorption; Montmorillonite; Solid acid catalyst

## 1. Introduction

Supported inorganic reagents are rapidly emerging as a new and environmentally accepted materials for improving process efficiency or to replace environmentally unacceptable reagents and catalysts [1]. Synergistic effects between the support materials and the reagents can lead to unexpectedly high activity. Replacement of environmentally unacceptable anhydrous AlCl<sub>3</sub>, an efficient catalyst for Friedel–Crafts reactions, by metal salt supported K-10-Mont (acid treated) has been claimed [2–4]. Supported ZnCl<sub>2</sub>-K-

10-Mont clay, known as “Clayzic”, is an important solid acid catalysts for certain Friedel–Crafts reactions despite the low activity of the individual component [5]. Exchange of interlayer Na<sup>+</sup> of smectite (Mont) by high charge density cations such as Al<sup>3+</sup>, Zn<sup>2+</sup>, etc. leads to acidity as high as 10 mol dm<sup>-3</sup>. These highly acidic forms of Mont clay have been described as broad spectrum catalysts for organic synthesis [1,6]. Such clays at high temperature reduce to Lewis acidity through the loss of interlayer water. It, therefore, appears that suitable supported metal ion or metal salt on Mont clay may play a key role as solid acid catalysts. In the present work, a systematic study on the Friedel–Craft reaction, e.g. benzylation of benzene using anhydrous metal salts (ZnCl<sub>2</sub>, CuCl<sub>2</sub> and NiCl<sub>2</sub>); metal exchange Mont (Zn<sup>2+</sup>-Mont, Cu<sup>2+</sup>-Mont and

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Ni<sup>2+</sup>-Mont) and metal salt supported on metal exchanged Mont (ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont, CuCl<sub>2</sub>-Cu<sup>2+</sup>-Mont and NiCl<sub>2</sub>-Ni<sup>2+</sup>-Mont) as solid acid catalysts have been carried out. The catalysts were characterized by X-ray diffraction (XRD) and thermal analysis.

## 2. Experimental

### 2.1. Materials and methods

Mont clay collected from Crook County, Wyoming, USA (Swy-2) source clay minerals repository, contained silica sand, iron oxide, etc. as impurities and was purified by the sedimentation methods [7]. The <2 μm fraction rich in Mont was collected. The oxide composition of the clay was SiO<sub>2</sub>: 58.12; Al<sub>2</sub>O<sub>3</sub>: 18.93; Fe<sub>2</sub>O<sub>3</sub>: 4.63; MgO: 2.52; CaO: 1.12; LOI: 13.54 and others 1.14%.

The clay was converted to the homoionic Na-exchanged form (Na<sup>+</sup>-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 dialyzate approached that of distilled water. The cation exchange capacity (CEC) of the clay was determined [8] and found to be 90 meq/100 g of clay.

### 2.2. Preparation of dry metal chloride

The dry metal chlorides were prepared by known SOCl<sub>2</sub> reflux method [9].

### 2.3. Preparation of cation-exchanged clay catalysts

M<sup>n+</sup>-Mont (M<sup>n+</sup> = Cu<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>) was prepared by the treatment of 3 g of Na<sup>+</sup>-Mont dispersed in 300 ml of distilled water with slow addition of 3 ml of 1 M solution of CuCl<sub>2</sub> or NiCl<sub>2</sub> or ZnCl<sub>2</sub>. The slurry was set aside for a few hours and dialysed against distilled water till the test of chloride was found to be negative and the conductivity of the dialyzate approached that of distilled water. The samples were collected and dried at 80 °C for 24 h [10–12].

### 2.4. Preparation of supported (1.5 mmol) metal salts-M<sup>n+</sup>-Mont catalyst

About 1 mmol of M<sup>n+</sup>-Mont was dispersed in 100 ml of water and stirred for about 2 h. 1.5 ml of

1 M metal chloride solution was added slowly and stirred for about 12 h. The slurry was dried in an oven at about 80 °C.

### 2.5. Activation of the catalysts

ZnCl<sub>2</sub>, Zn<sup>2+</sup>-Mont and ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont were activated under dry air at 120, 150 and 250 °C for 8 h.

### 2.6. Measurement of surface acidity (active acid sites) of the catalyst by ammonia adsorption method [13,14]

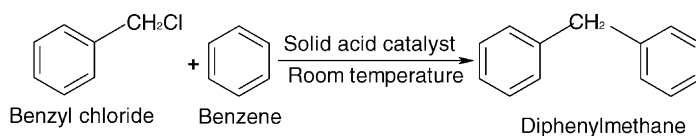
The catalysts were thermally activated at 150 °C under flowing nitrogen for 1 h. Ammonia gas was then purged for 2 h. The nature and strength of acidic sites were determined from the desorption of chemisorbed ammonia by thermogravimetric analysis (TGA) (TA instrument, Model STD 2960 simultaneous DTA–TGA) in the temperature range 150–700 °C. The surface acidity was further substantiated by differential scanning calorimeter (DSC) of ammonia presorbed activated samples using the equipment DSC/SDT-2960 M/S TA corporation, USA.

### 2.7. Basal spacing determination by XRD technique

Basal spacing (*d*<sub>001</sub>) of the samples were determined from the oriented sample prepared on glass slides by standard techniques [15]. XRD patterns of the samples heated at different temperatures were taken in the range 2θ = 2–60° at a rate of 6° min<sup>-1</sup> (X-ray Diffractometer Jeol, JDX-11P3A, Japan).

### 2.8. General procedure for the benzylation of benzene

The reaction was carried out in a 25 ml round bottom flask with CaCl<sub>2</sub> guard tube. Dry benzyl chloride (1.25 ml), 25 ml of dry benzene and required amount of catalyst were taken into the flask. The substrate (benzyl chloride) to metal (content in catalysts Zn<sup>2+</sup>-Mont, ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont, etc.) was in 1:0.17 mol ratio. The mixture was then stirred at room temperature by a magnetic stirrer at 300 rpm. The reaction products were taken after 0.25, 0.75, 2, 5,



Scheme 1.

10, 18, 24, 48 and 72 h interval of reaction and were analyzed by GC (Chemito GC, Model 8510, FID).

### 3. Results and discussions

Preliminary studies on benzylation of benzene (Friedel–Crafts reaction) to produce diphenylmethane (Scheme 1) in presence of different solid acid catalysts like anhydrous metal salts  $MCl_2$ ,  $M^{n+}$ -Mont and  $MCl_2$ - $M^{n+}$ -Mont ( $M = Cu, Ni, Zn; n = 2$ ) reveal that  $Zn^{2+}$ -Mont and  $ZnCl_2$ - $Zn^{2+}$ -Mont exhibit high catalytic activities (Fig. 1) and the rest show either low or negligible activities and therefore, detail study has been concentrated only on these two composites and further catalytic activities of Cu and Ni

containing composites were not performed. The reason for such low activities is attributed to poor acidity of the composites. It is observed (Fig. 1) that during the initial period of the reaction the catalytic activity of  $ZnCl_2$ - $Zn^{2+}$ -Mont was very low which increased gradually and near 48 h of reaction the catalytic activity became almost same as that of  $Zn^{2+}$ -Mont composite.

#### 3.1. Characterization of the composites

##### 3.1.1. Thermal desorption and differential scanning calorimetric technique for overall acidity determination

The desorption of adsorbed ammonia by  $Zn^{2+}$ -Mont and  $ZnCl_2$ - $Zn^{2+}$ -Mont composites were studied by

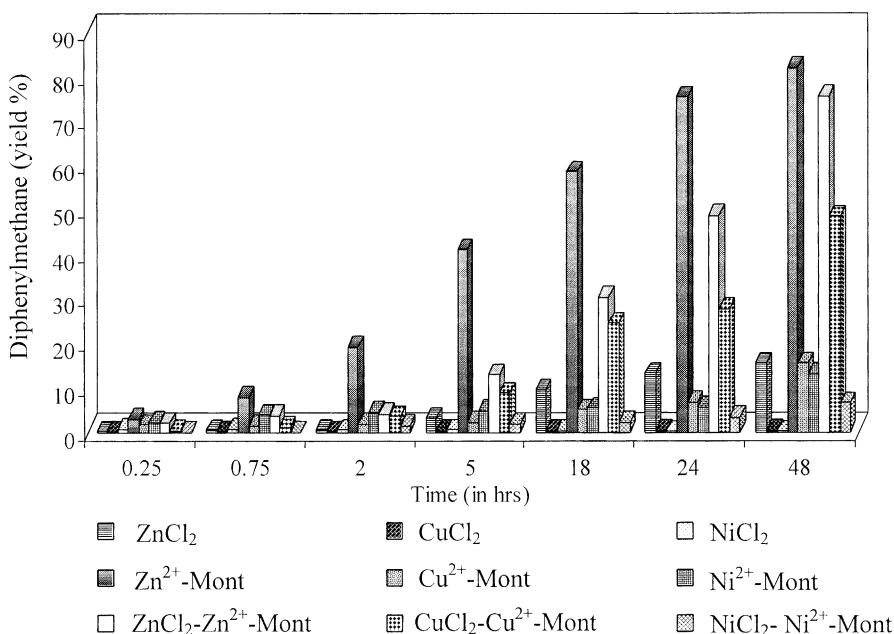


Fig. 1. The percentage conversion of diphenylmethane in benzylation of benzene at room temperature using different catalysts (1.5 mmol catalyst, activation temperature 120 °C).

thermogravimetric analysis in the temperature range 25–700 °C (TA Instrument, Model STD 2960 simultaneous DTA–TGA). From room temperature up to about 150 °C (Fig. 2a) the composites show almost no loss of mass (TG peaks) as the samples were generated at about 150 °C. Above 150 °C, two distinct peaks of TG are obtained for the  $\text{NH}_3\text{-Zn}^{2+}\text{-Mont}$  in the temperature range 200–380 and 450–650 °C with corresponding mass loss of 1.62 and 5.19%. While  $\text{Zn}^{2+}\text{-Mont}$  composite shows the corresponding mass loss of 1.40 and 3.20% (Fig. 2b). The DTA curve shows a broad exothermic peak in the same temper-

ature range (Fig. 2a and b). The additional mass loss in  $\text{NH}_3\text{-Zn}^{2+}\text{-Mont}$  in the temperature regions, i.e. 200–380 and 450–650 °C have been attributed to the desorption of ammonia from Bronsted and Lewis acid sites, respectively. Therefore, the amount of desorption of  $\text{NH}_3$  equivalent to Bronsted and Lewis acid sites were found to be 0.129 and 1.17 mmol  $\text{g}^{-1}$  of the  $\text{Zn}^{2+}\text{-Mont}$  composite.

In case of  $\text{ZnCl}_2\text{-Zn}^{2+}\text{-Mont}$  three distinct mass loss (Fig. 2c) of 4.2, 5.3 and 2.5% are observed in the temperature range 150–425, 425–620 and 640–700 °C, respectively. While for  $\text{NH}_3\text{-ZnCl}_2\text{-Zn}^{2+}\text{-}$

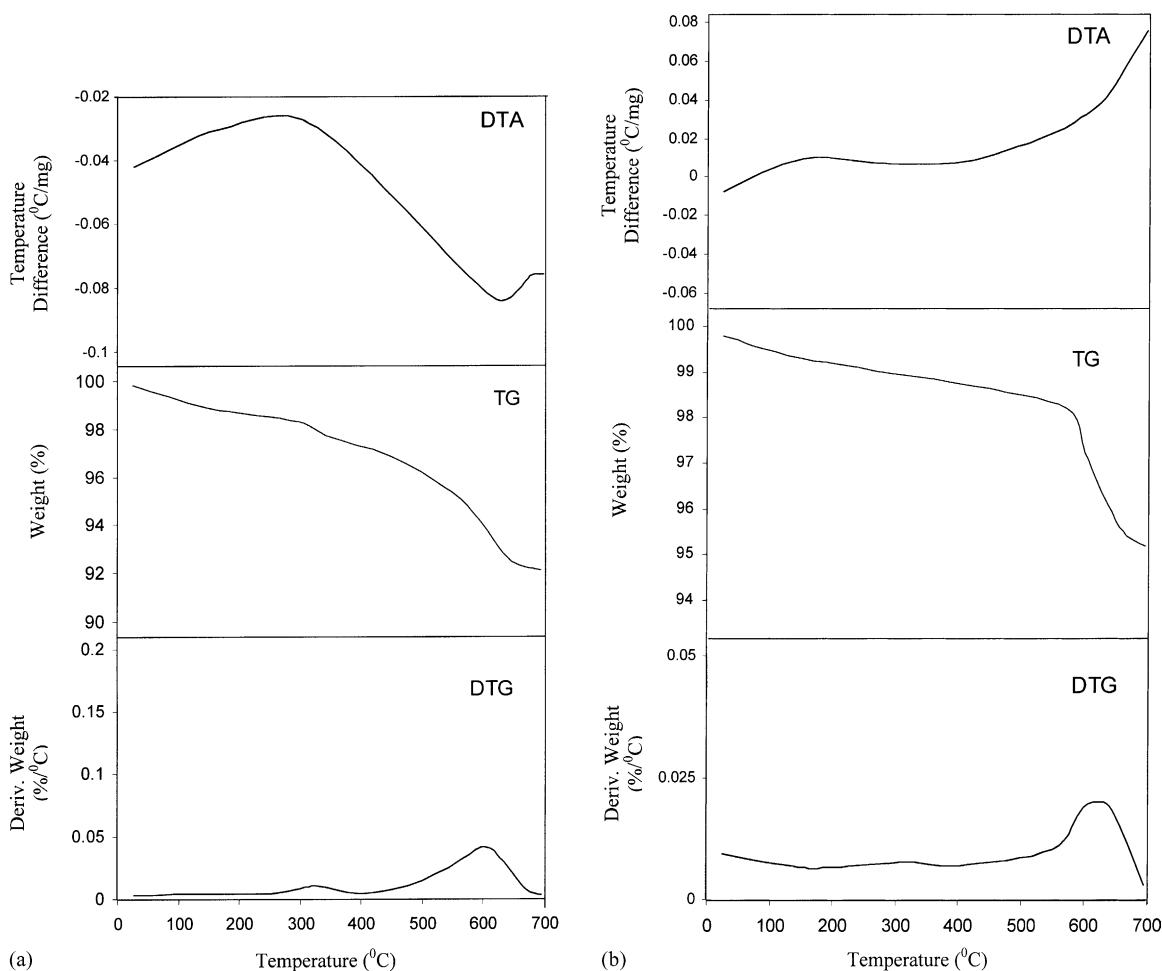


Fig. 2. (a) Thermal analysis of  $\text{NH}_3$  adsorbed  $\text{Zn}^{2+}\text{-Mont}$  preheated at 150 °C; (b) thermal analyses of  $\text{Zn}^{2+}\text{-Mont}$  1.5 mmol preheated at 150 °C; (c) thermal analyses of  $\text{ZnCl}_2\text{-Zn}^{2+}\text{-Mont}$  1.5 mmol preheated at 150 °C; (d) thermal analyses of  $\text{NH}_3$  adsorbed  $\text{ZnCl}_2\text{-Zn}^{2+}\text{-Mont}$  preheated at 150 °C.

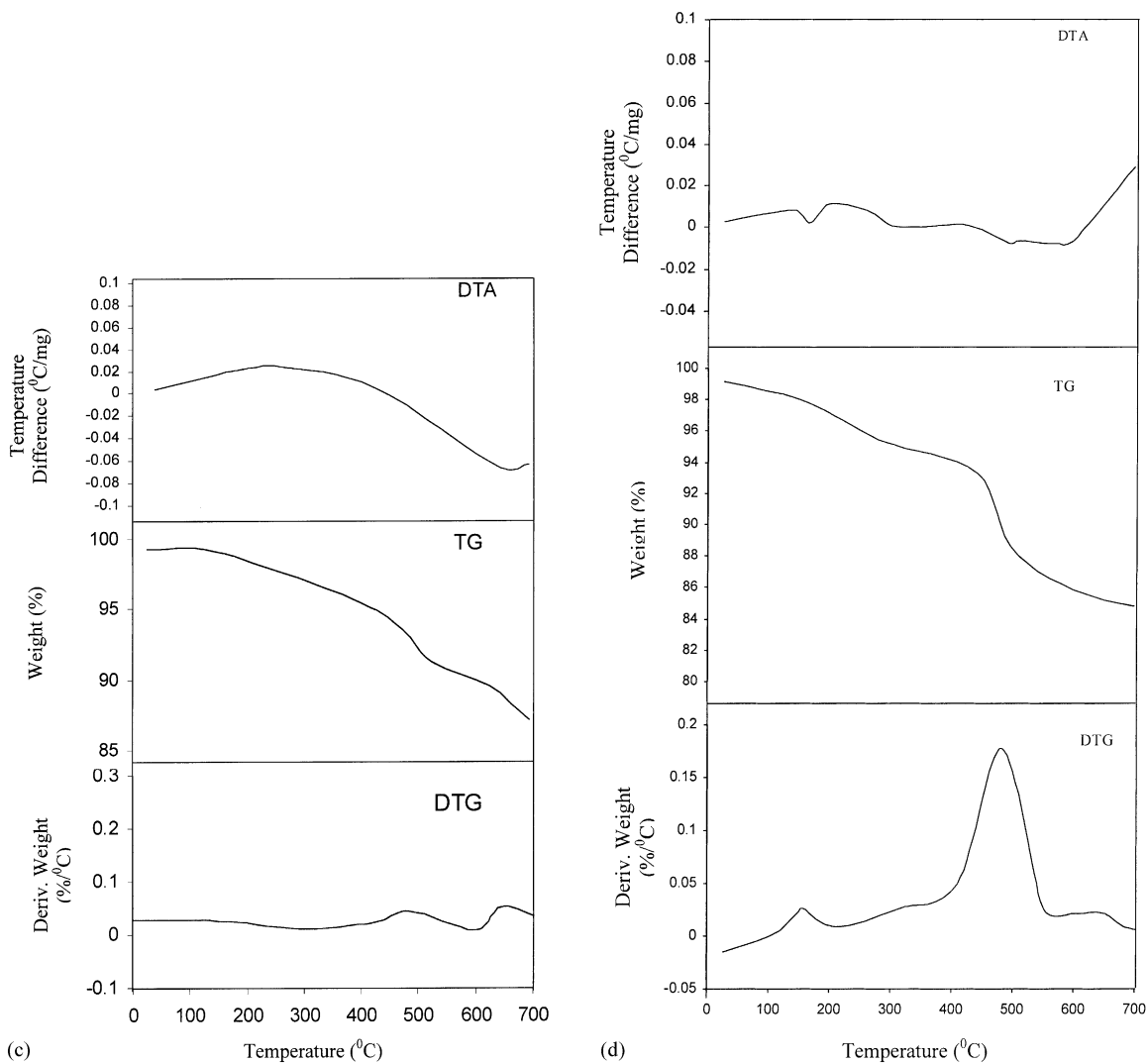


Fig. 2. (Continued).

Mont shows (Fig. 2d) two distinct mass loss of 4.7 and 8.3% for the temperature range 150–440 and 440–680 °C, respectively. The loss of NH<sub>3</sub> thus amounts to 0.647 and 1.705 mmol g<sup>-1</sup> for the Bronsted and Lewis acid sites, respectively. The DTA curves (Fig. 2c) show one very broad and strong and one weak peak in the range 150–635 and 640–700 °C for the composite ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont. In case of NH<sub>3</sub>-ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont, the DTA curve shows (Fig. 2d) three endothermic peaks at 157, 300, and 495 °C and two exothermic peaks at 230 and 428 °C.

Thus, it appears that the amount of Lewis acid sites is much higher than the Bronsted acid sites in both the composites, i.e. Zn<sup>2+</sup>-Mont and ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont, and the later composite show higher acid sites than the former. Therefore, it is likely that the ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont composite should show higher acid catalyst activity than the Zn<sup>2+</sup>-Mont composite.

The differential scanning calorimetric thermograms of the different composites are shown in the Fig. 3. The NH<sub>3</sub>-Zn<sup>2+</sup>-Mont shows (Fig. 3a) two exothermic broad peaks in the temperature range 160–410

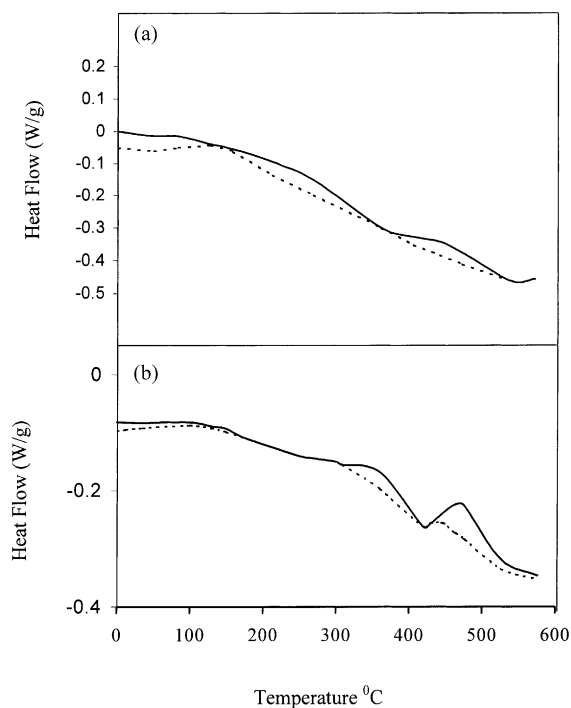


Fig. 3. (a) (—) DSC of NH<sub>3</sub> adsorbed Zn<sup>2+</sup>-Mont preheated at 150 °C for 2 h, (---) DSC of Zn<sup>2+</sup>-Mont preheated at 150 °C for 2 h; (b) (—) DSC of NH<sub>3</sub> adsorbed ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont; preheated at 150 °C for 2 h, (---) DSC of ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont preheated at 150 °C for 2 h.

and 415–540 °C attribute to desorption of NH<sub>3</sub> from the Bronsted and Lewis acid sites, respectively, while no such peaks are observed in case of Zn<sup>2+</sup>-Mont composite. Similarly, NH<sub>3</sub>-ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont exhibits (Fig. 3b) two distinct broad exothermic peaks in the temperature range 320–430 and 450–580 °C indicating NH<sub>3</sub> has been chemisorbed on the Bronsted and Lewis acid sites, respectively. The neat ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont (Fig. 3b) on the other hand shows no such peaks. These data corroborate the observations of TG/DTA studies.

### 3.1.2. X-ray diffraction studies

The basal spacings ( $d_{001}$ ) of the composites Zn<sup>2+</sup>-Mont and ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont are shown in Fig. 4. It appears that at room temperature the  $d_{001}$  value of Zn<sup>2+</sup>-Mont, i.e. 15.2 Å decreases gradually and finally reaches a value of 10.28 Å at about 250 °C. Similarly, the ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont shows a gradual

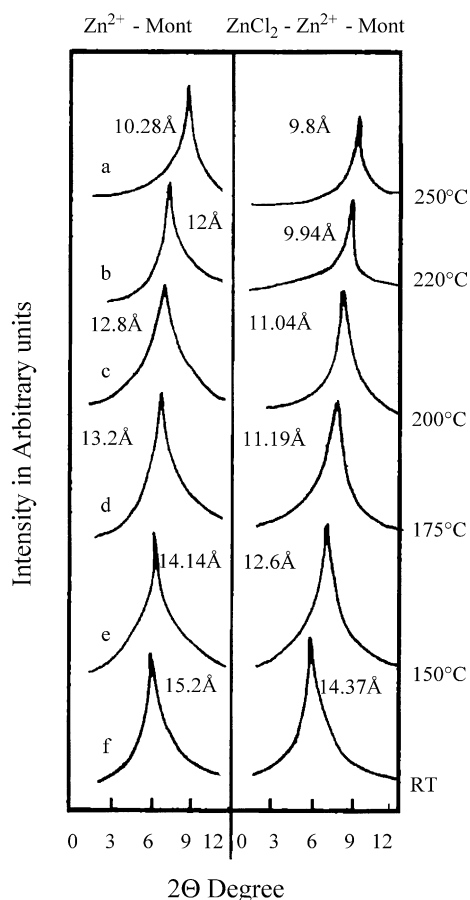


Fig. 4. Basal spacing of the composites Zn<sup>2+</sup>-Mont and ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont heated at different temperatures.

lowering of its basal spacing  $d_{001}$  of 14.37 Å (room temperature) to about 9.8 Å at 250 °C. Therefore, it has become obvious that the Zn<sup>2+</sup>-Mont composite heated at 150 °C (optimum activation temperature) shows higher basal spacing (14.14 Å) than that of ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont (12.6 Å). Thus, it may suggest that the Zn<sup>2+</sup>-Mont composite is likely to act as more efficient solid acid catalysts than the ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont composite for organic reactions because of higher interlayer spacing.

### 3.1.3. Effect of ZnCl<sub>2</sub> loading on the activity of catalyst

The effect of loading of ZnCl<sub>2</sub> on Zn<sup>2+</sup>-Mont support against the percentage yield of diphenyl-

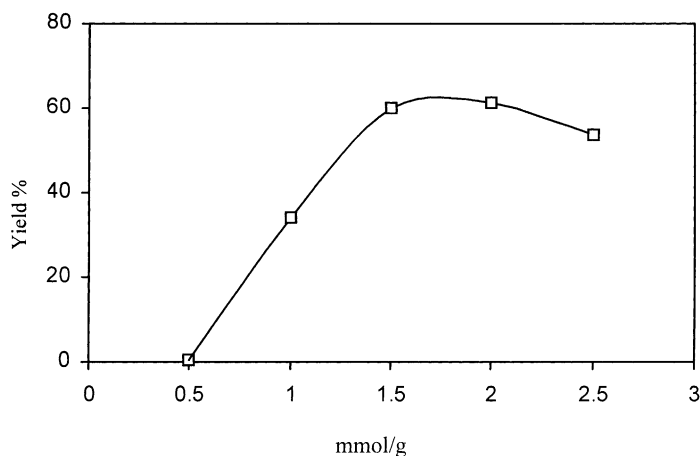


Fig. 5. Effect of different loading on the percentage yield of diphenylmethane up to 8 h reaction using  $\text{ZnCl}_2\text{-Zn}^{2+}\text{-Mont}$  catalyst activated at  $150^\circ\text{C}$ .

methane is shown in Fig. 5. It appears that at a loading of  $0.5\text{ mmol g}^{-1}$ , the amount of conversion is negligible. On increasing the amount of loading, the conversion increases and reaches a maximum at about  $1.5\text{ mmol g}^{-1}$ . Further increase of loading at  $2.5\text{ mmol g}^{-1}$ , the rate of conversion decreases. Thus, the amount of loading of  $\text{ZnCl}_2$  on  $\text{Zn}^{2+}\text{-Mont}$  plays an important role for acting as acid catalyst.

#### 3.1.4. Effect of activation temperature on catalytic activity

The effect of different activation temperature on the percentage yield of diphenylmethane using  $\text{Zn}^{2+}\text{-Mont}$  and  $\text{ZnCl}_2\text{-Zn}^{2+}\text{-Mont}$  catalyst are shown in Fig. 6. It reveals that at activation temperature of  $120^\circ\text{C}$  the conversion were 58.52 and 30.30% for  $\text{Zn}^{2+}\text{-Mont}$  and  $\text{ZnCl}_2\text{-Zn}^{2+}\text{-Mont}$ , respectively and enhances to 95.0 and 91.51% on increasing activation temperature to about  $150^\circ\text{C}$  for a reaction time of 18 h at room temperature. On increasing the temperature further up to  $250^\circ\text{C}$  the corresponding yields were 66 and 38%. Therefore, the optimum temperature is around  $150^\circ\text{C}$ . The activation temperature of the catalysts plays an important role over basal spacing of the catalysts as it is revealed from the fact that the basal spacing of the catalysts is higher at  $120^\circ\text{C}$  (not shown in Fig. 4) than at  $150^\circ\text{C}$ , but the activity of the acid sites activated at  $120^\circ\text{C}$  are lower than that done at  $150^\circ\text{C}$  (Figs. 1, 6 and 7).

#### 3.1.5. The yield of diphenylmethane against time

The percentage yield (Fig. 7) of diphenylmethane in presence of  $\text{Zn}^{2+}\text{-Mont}$  ( $1.5\text{ mmol}$ ,  $3.33\text{ g}$ ) and  $\text{ZnCl}_2\text{-Zn}^{2+}\text{-Mont}$  ( $1.5\text{ mmol}$ ,  $0.926\text{ g}$ ) against time indicate that within a period of 15 min, the yields were 6.8 and 1.0% for  $\text{Zn}^{2+}\text{-Mont}$  and  $\text{ZnCl}_2\text{-Zn}^{2+}\text{-Mont}$ , respectively. With the increase in reaction time, appreciable conversions were obtained, i.e. within 5 h of reaction time the corresponding yields were 78.72 and 45.88%, respectively which enhance to 97.6 and

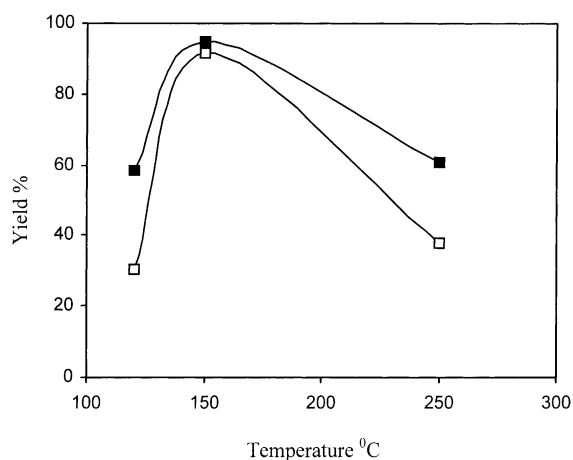


Fig. 6. The effect of activation temperature on the percentage yield of diphenylmethane using  $\text{Zn}^{2+}\text{-Mont}$  (■) and  $\text{ZnCl}_2\text{-Zn}^{2+}\text{-Mont}$  (□) catalysts ( $1.5\text{ mmol Zn}^{2+}$  content) at 18 h of reaction.

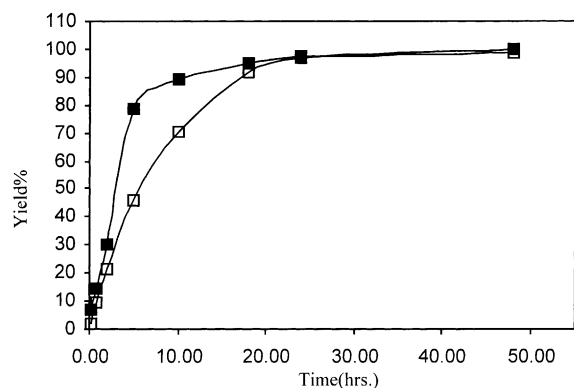


Fig. 7. The percentage yield of diphenylmethane in presence of Zn<sup>2+</sup>-Mont (■) and ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont (□) catalysts (1.5 mmol/g loading at 150 °C activation temperature) against reaction time at room temperature.

96.7% near 24 h. The selectivity in such reaction products are greater than 98%. On further increasing the reaction time to 48 h, 100 and 98% conversion for the respective composites were observed. It is interesting to indicate here that during the initial period of the catalytic reaction, the activity of Zn<sup>2+</sup>-Mont composite is higher than ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont though the latter exhibits higher amount of acid sites (Fig. 2a and d). The higher catalytic activity is attributable to the higher pore volume of the composite Zn<sup>2+</sup>-Mont (0.032 cm<sup>3</sup> g<sup>-1</sup>) than that of ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont (0.011 cm<sup>3</sup> g<sup>-1</sup>). Thus, it indicates that the amount of acid sites is not always the indicative parameter for higher catalytic activity. During the later part of the reaction, the activity of the ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont increases and becomes almost equal as that of Zn<sup>2+</sup>-Mont which indicates that much activation of the acid sites occur in the former composite. It may be mentioned here that the composites do not show any leaching of Zn<sup>2+</sup> in the liquid phase. The catalysts are reusable. After the catalytic experiments, the recovered catalysts are activated at desired temperature (150 °C). The second and third run indicate negligible loss of activity of the catalysts.

### 3.1.6. Benzylation of benzene with benzyl chloride

The percentage yields of benzylation of benzene to diphenylmethane against time in presence of different catalysts at room temperature are shown in Fig. 1. The results obtained indicate (Fig. 1) that, in

general, the percentage yields in the benzylation of benzene increases with time irrespective of the nature of the catalyst activated at 120 ± 10 °C. Further, it has been observed that the anhydrous metal salts catalysts, namely ZnCl<sub>2</sub>, CuCl<sub>2</sub> and NiCl<sub>2</sub> show the lowest activity. In case of ZnCl<sub>2</sub> only about 12% conversion occurred even up to a period of 48 h while activity in the case of the other two salts has been found to be negligible. However, the conversion in presence of the metal-Mont catalysts has been found to be higher than that with the anhydrous metal salts catalysts alone. Zn<sup>2+</sup>-Mont among others has been found to show the highest conversion of about 80% within a period of 48 h while Cu<sup>2+</sup>-Mont and Ni<sup>2+</sup>-Mont show 16 and 14% conversion, respectively. Amongst the metal-salt-metal-Mont catalysts, ZnCl<sub>2</sub>-Zn<sup>2+</sup>-Mont has shown conversion of 76% where as CuCl<sub>2</sub>-Cu<sup>2+</sup>-Mont and NiCl<sub>2</sub>-Ni<sup>2+</sup>-Mont have shown only 48 and 6.4% conversion, respectively.

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### References

- [1] J.H. Clark, *Catalysis of Organic Reactions by Supported Inorganic Reagents*, VCH Publishers, New York, 1994.
- [2] J.H. Clark, K. Martin, A.J. Teasdale, S.J. Barlow, *J. Chem. Soc. Chem. Commun.* (1995) 2037.
- [3] C.N. Rhodes, M. Franks, G.M.B. Parkes, B.R. Brown, *J. Chem. Soc. Chem. Commun.* (1991) 804.
- [4] J.H. Clark, A.P. Kybett, D.J. Macquarrie, S.J. Barlow, P. Landon (in part), *J. Chem. Soc. Chem. Commun.* (1989) 1353.
- [5] J.H. Clark, S.R. Cullen, S.J. Barlow, T.W. Bastck, *J. Chem. Soc. Parkin 2* (1994) 117.
- [6] J.A. Ballantine, J.H. Punell, J.M. Thomas, *J. Mol. Catal.* 27 (1984) 157.
- [7] J.E. Gillot, *Clay in Engineering Geology*, first ed., Elsevier, Amsterdam, 1968 (Chapter II).



- [8] A.B. Searle, R.W. Grimshaw, *The Chemistry and Physics of Clays and Other Ceramic Materials*, third ed., Earnest Benn., London, 1960 (Chapter V).
- [9] T. Moeller (Ed.), McGraw Hill Book Company, vol. 5, London, 1957, p. 153.
- [10] P. Lazlo, A. Mathy, *Helvetica Chemica. Acta.* 70 (1987) 577.
- [11] J. Tateiwa, S. Uemura, *Sekiyu. Gakkaishi* 40 (1997) 329.
- [12] J. Tateiwa, A. Kimura, M. Takasuka, S. Uemura, *J. Chem. Soc. Parkin Trans.* 1 (1997) 2169.
- [13] D.R. Brown, C.N. Rhodes, *Catal. Lett.* 45 (1997) 35.
- [14] J. Tateiwa, H. Horiuchi, K. Hashimoto, T. Yamauchi, S. Uemura, *J. Org. Chem.* 59 (1994) 5901.
- [15] G.W. Brindley, G. Brown, *Crystal Structure of Clay Minerals and their X-ray Identification*, Mineralogical Society, Monograph No. 5, London, 1984 (Chapter 5).