

Role of clay as catalyst in Friedel–Craft alkylation

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Abstract. Solid acids have become increasingly important for many liquid-phase industrial reactions these days. Montmorillonite clays (2:1 clay mineral) have been used as efficient solid acid catalysts for a number of organic and liquid phase reactions and offer several advantages over classic acids. Tailor made catalysts can be prepared from clays by suitably adjusting their acidity and surface area by acid activation. In the present work, preparation, characterization and performance of Pt (II) clays, Cu (II) clays, acid clay, and sol–gel hybrids of Cu (II) clays as solid catalysts in a test Friedel–Craft alkylation reaction of benzyl chloride with toluene using differential scanning calorimeter (DSC) are reported. Product formation has been analysed by FTIR spectroscopy. The main objective of this work is to show how clay as a solid catalyst affects reaction rates and activation energies. Acidity and dispersion of solid catalysts are two main factors which govern a catalysis reaction. Kinetic parameter analysis and XRD studies confirm that acid Pt (II) clay and Pt (II) clay dispersed by natural dispersants are more effective catalysts. In contrast to the reactions using AlCl_3 , the experimental conditions are non-polluting and the final work up does not require any aqueous treatment.

Keywords. Montmorillonite clay; exfoliation; sol–gel process; Friedel–Craft alkylation; DSC.

1. Introduction

Clays are molecularly engineered aluminium/magnesium silicates having 1:1 or 2:1 layer structures. Natural clays possess various uses and applications. It is thermally inert and environmental friendly. Clay has unique properties such as high aspect ratio (Van Es 2003), ease of delamination, due to which it finds application in processing of active components, binders, catalysts, as ion-exchanger for food processing, additives in detergents, thickening agents in oil drilling operation (Coombes *et al* 2003). Besides these, clay is a key component of soil and plays a crucial role in agriculture, potteries and ceramics (Coombes *et al* 2003). Clay derived catalysts find application in removal of nitrogen oxides, encompassing both cationic and anionic materials (Sirilumpen *et al* 1999; Serwicka 2001; Belver *et al* 2004; Gryzbek 2007).

In 2:1 clay minerals, tetravalent Si in tetrahedral sheet is sometimes partly replaced by trivalent Al. In the octahedral sheet, there may be replacement of trivalent Al by divalent Mg. This replacement is often referred to as isomorphous substitution (Van Olphen 1963). Due to this, deficit of positive charge takes place or in other words excess of negative charge. The excess of negative charge is compensated by the adsorption on the layer surfaces of cation which are too large to be accommodated in the interior of crystal. In the presence of water, the compensating cations on the layer surfaces may

be easily exchanged by other cations when available in solution, hence they are called exchangeable cations. Thus clay minerals bear potential of forming hybrid materials.

Catalytic technologies play a key role in the economic development and growth of the chemicals industry and contributes to around 20% of world GNP (Wilson and Clark 2000). Release of waste and toxic emissions has serious implications of the chemicals industry, leading to environmental pollution which is a challenge these days. Thus the need of the hour is to implement ‘clean technology’ inducing the use of alternative heterogeneously catalyzed processes (Wilson and Clark 2000; Yadav and Doshi 2002). Thus solid acids have become increasingly important for many liquid-phase industrial reactions these days (Gronnow and Macquarrie 2005).

Montmorillonite clays (2:1 clay mineral) have been used as an efficient solid acid catalyst for a number of organic and liquid-phase reactions and offer several advantages over classic acids: strong acidity, non-corrosivity, cheapness, mild reaction conditions, high yield and selectivity, ease of set up and work up, possess comparatively strong acid sites (H_0 typically between -5.6 and -8.2) and partly amorphous nature provides mesoporosity over a wide range of pore sizes (Zhang *et al* 1997; Wang *et al* 1998; Hart and Brown 2004). Tailor made catalysts can be prepared from clays by suitably adjusting their acidity and surface area by acid activation (Pushpaletha *et al* 2006).

In the present work, Pt (II) clays, Cu (II) clays, acid clay, and sol–gel hybrid materials of Cu (II) clay have been

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prepared and their catalytic effect over Friedel–Craft alkylation reaction of benzyl chloride with toluene has been studied using DSC. Product formation has been analysed by FTIR spectroscopy. Activation energies, rate of reactions and turn over frequency (TOF) of catalyst samples have been studied involving kinetic parameter analysis. Delamination of clay platelets leading to dispersion of the catalyst samples was studied using XRD. Charge properties of catalyst samples were measured by Zeta Meter.

2. Experimental

2.1 Preparation of Pt (II) clay

2.1a Materials: Clay used in this experiment was montmorillonite KSF which was obtained from Fluka Chemie AG, Switzerland. Chloroplatinic acid and cetyl trimethyl ammonium bromide (CTAB) were obtained from Ranbaxy Chemicals Ltd., India. Natural dispersant was obtained from natural source.

2.1b Method: The clay was impregnated with $[\text{Pt}^{\text{II}}(\text{NH}_3)_4]\text{Cl}_2$ precursor following a wet impregnation method with a solution/support ratio of 25 ml/g. The amount of precursor dissolved in the impregnating solution was 2.3 wt% (Vicente and Lambert 2001).

The above procedure was applied to make Pt (II) clay disperse in natural dispersant (T704–2), Pt (II) clay disperse in CTAB (T704–3), acid Pt (II) clay (T704–1), and pure Pt (II) clay (T704–4). 0.5 g clay was suspended in 6.25 ml of water. 2.3 wt% of $[\text{Pt}^{\text{II}}(\text{NH}_3)_4]\text{Cl}_2$ precursor (0.0115 g) was weighed and dissolved in 6.25 ml of water. It was then added to clay suspension. The resulting solution was then stirred vigorously for a few hours, centrifuged and washed several times until negative chloride test was obtained. The samples were then dried at room temperature.

2.2 Preparation of Cu (II) clay

2.2a Materials: Montmorillonite KSF used in the experiment was obtained from Fluka Chemie AG, Switzerland. Cetyl trimethyl ammonium bromide, and NaOH were obtained from Ranbaxy Chemicals Ltd., India. Cupric acetate was obtained from S D Fine Chemicals Ltd., India.

2.2b Method: 0.1 M Cu-acetate in 0.1 M NaOH (OH/Cu=1:2) was added to clay suspension in water and stirred for several hours. The solid was then extracted by centrifugation, washed with water several times and dried in an oven (Sun Kou *et al* 2003). The above procedure was applied to prepare Cu (II) clays taking two clays (i) clay dispersed by natural dispersant (T606–11) and (ii) clay dispersed by CTAB (T606–12).

2.3 Preparation of sol–gel material of Cu (II) clay

2.3a Materials: Cu clays dispersed in natural dispersant, CTAB. Ti isopropoxide was obtained from Fluka Chemie AG, Switzerland. Isopropanol was obtained from Ranbaxy Chemicals Ltd., India.

2.3b Method: Equal amounts of Ti isopropoxide and water (stirred for 1 min) were mixed and isopropanol was added to prevent coagulation and stirred till clear solution formed. Clay suspension was then added dropwise, stirred for 4–5 h till whole clay got fully dispersed in solution. The resulting product was centrifuged and dried using blotting paper (Jordens 1999). The materials were sol–gel materials of (i) Cu (II) clay dispersed by natural dispersant (T606–15) and (ii) Cu (II) clay dispersed by CTAB (T606–14).

2.4 Preparation of acid clay

2.4a Materials: Clay used in this experiment was Montmorillonite KSF, which was obtained from Fluka Chemie AG, Switzerland. HCl was obtained from Ranbaxy Chemicals Ltd., India.

2.4b Method: Montmorillonite clay was heated in a furnace till 700°C and quenched immediately in 0.1 N HCl after taking the sample out of the furnace. The resulting sample was centrifuged and dried at room temperature.

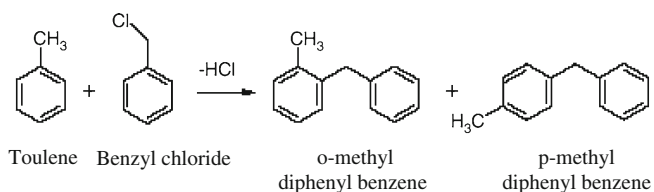
2.5 Instrumentation

DSC of Friedel–Craft alkylation reaction over various clay catalysts was performed on Differential Scanning Calorimeter Perkin Elmer DSC-7 under nitrogen atmosphere at a scan rate of 20°C/min. IR spectra of the samples were recorded using Perkin Elmer FTIR Spectrometer Spectrum 2000. Zeta potential of the samples was measured using Zeta-Meter 3.0+ with microscope type GT2 cell N° 3519, size 0.0 k: 65. XRD data of various clay catalyst samples were obtained using X'Pert Software, Phillips, powder diffractometer equipped with Cu-K α generator ($\lambda = 1.5405600$). Generator tension was 35 kV.

3. Results and discussion

Friedel–Craft alkylation of benzyl chloride with toluene over the following clays as catalyst was carried out using DSC instrument as shown in scheme 1.

(i) Pt (II) clay (T704–4), (ii) Pt (II) clay where clay is dispersed by natural dispersant (T704–2), (iii) Pt (II) clay where clay is dispersed by CTAB (T704–3), (iv) acid Pt (II) clay (T704–1), (v) montmorillonite clay (T703–15), (vi) Cu (II) clay where clay is dispersed by natural dispersant (T606–11),



Scheme 1. Friedel-Craft alkylation of benzyl chloride with toluene.

(vii) Cu (II) clay where clay is dispersed by CTAB (T606–12) and (viii) sol–gel materials of Cu (II) clays (T606–14 and T606–15).

3.1 DSC analysis

Friedel–Craft alkylation reaction of benzyl chloride with toluene over AlCl_3 as catalyst, generally takes place at 85°C . When solid clay catalyst samples were used in place of AlCl_3 , significant changes in reaction were observed. The most efficient catalysts among Pt (II) clays were acid Pt (II) clay (T704–1) and Pt (II) clay dispersed by natural dispersant (T704–2) which showed exothermic peaks at 80°C . CTAB dispersed Pt (II) clay (T704–3) showed exothermic peak at 92°C , while Pt (II) clay (T704–4) and pure clay (T703–15) showed exothermic peaks at around 100°C and 110°C , respectively as evident from figure 1.

Among Cu (II) clays, CTAB dispersed Cu (II) clay (T606–12) and Cu (II) clay dispersed by natural dispersant (T606–11) showed exothermic peaks at 100°C and

85°C , respectively. Sol–gel material of CTAB dispersed Cu (II) clay (T606–14) showed exothermic peak at a temperature $> 125^\circ\text{C}$ while sol–gel material of Cu (II) clay dispersed by natural dispersant (T606–15) at a temperature slightly $< 125^\circ\text{C}$ as evident from figure 2.

Acidity of clay is a main factor for catalysis to take place. Among the various catalysts screened, acid Pt (II) clay and Pt (II) clay dispersed by natural dispersant were found to be more effective than others due to more number of acidic sites. When Cu (II) clay was used in place of Pt (II) clay, temperature range increases to 120°C . Cu incorporation in clay does not alter the basal spacing, surface area as well as porosity, but the total number of acidic sites dramatically decreases thus altering catalysis reaction. Sol–gel materials showed decreased catalytic activity due to formation of bulky material.

When the experiment was carried out in absence of reagent, as shown in figure 3 and in absence of clay as in figure 4, no such peaks were observed. It may be said that exothermic peak is due to the reaction being taking place at that temperature, with clay acting as a catalyst, and formation of product shown by two endothermic peaks indicating that one major and one minor product may have been formed. Products formed in this Friedel–Craft alkylation reaction are ortho-methyl diphenyl benzene and para-methyl diphenyl benzene.

3.2 IR analysis

FTIR spectra of catalyzed reaction product as in figure 5 show the following peaks. Besides all prominent peaks of

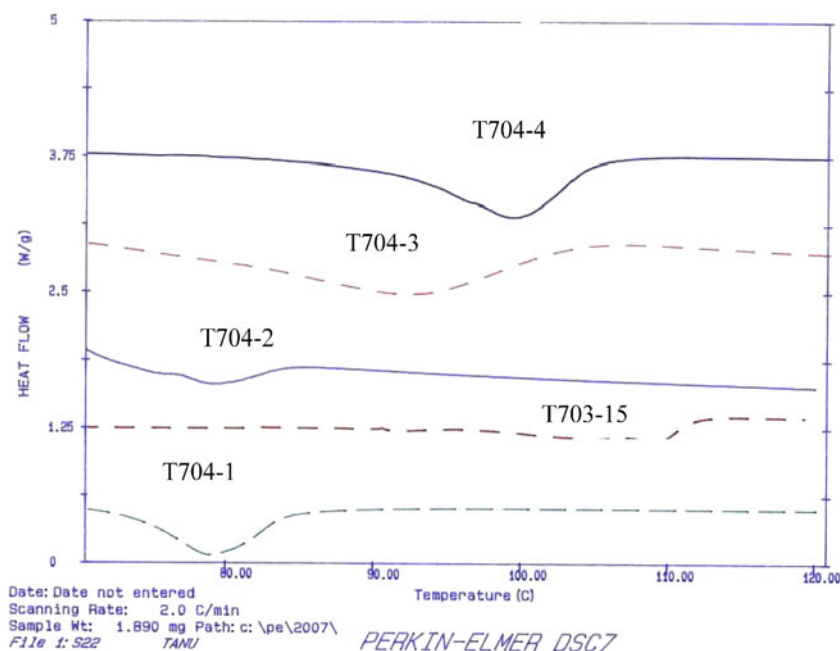


Figure 1. DSC thermograms of various Pt (II) clay catalyst samples.

clays i.e. Si–OH stretch between 3700 and 3200 cm^{-1} , Si–O–Si asymmetric stretch at 1043.64 cm^{-1} , Si–O–Si symmetric stretch at 805 cm^{-1} , Si–O–Si bend at 469.14 cm^{-1} , peaks of C–H stretch (aromatic) at 3099 cm^{-1} , 3068 cm^{-1} , 3032 cm^{-1} , C–H stretch (alkyl) at 2925 cm^{-1} , C–C stretches

in aromatic ring at 1614 cm^{-1} , 1506 cm^{-1} , 1465 cm^{-1} , characteristic overtones from 2000 – 1665 cm^{-1} , in plane C–H bending at 1035 cm^{-1} and 1086 cm^{-1} , out of plane C–H bending at 738 cm^{-1} are observed. Thus it can be said that formation of product may have taken place.

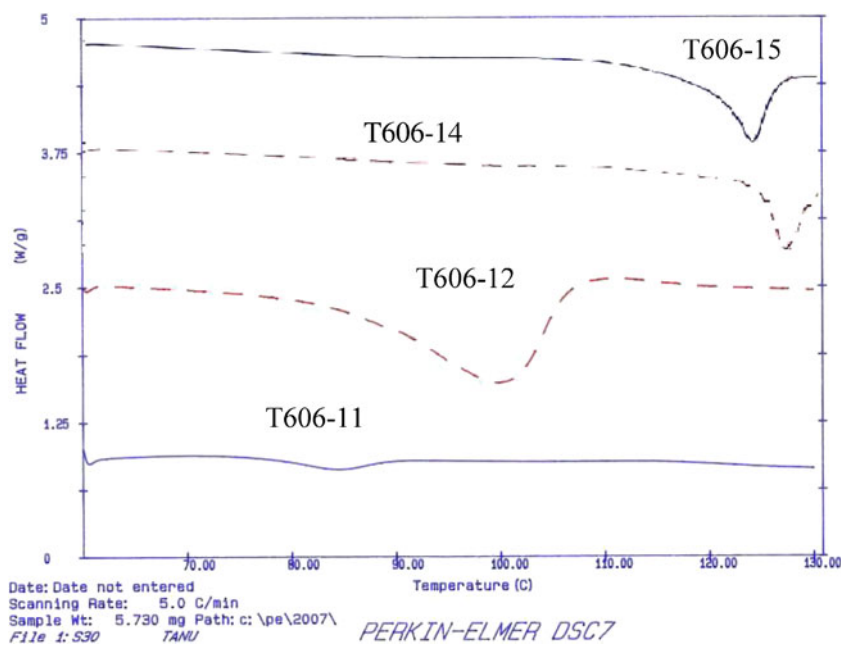


Figure 2. DSC thermograms of various Cu (II) clay catalyst samples.

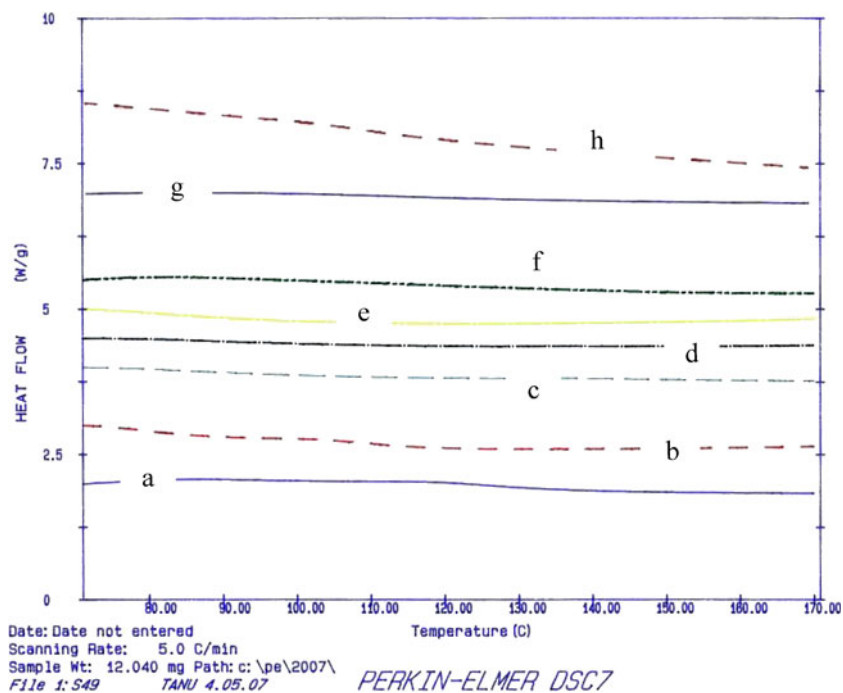


Figure 3. DSC thermograms of (a) T704–1, (b) T704–2, (c) T704–3, (d) T704–4, (e) T606–11, (f) T606–12, (g) T606–14 and (h) T606–15 in absence of reagent (benzyl chloride and toluene) in Friedel–Craft alkylation reaction.

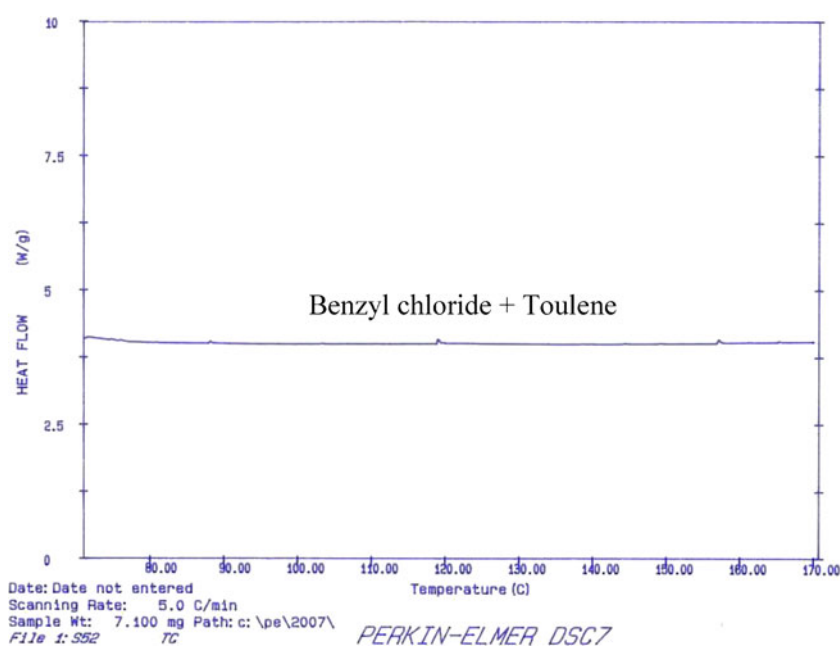


Figure 4. DSC thermogram of reagent in absence of clay catalyst in Friedel–Craft alkylation reaction.

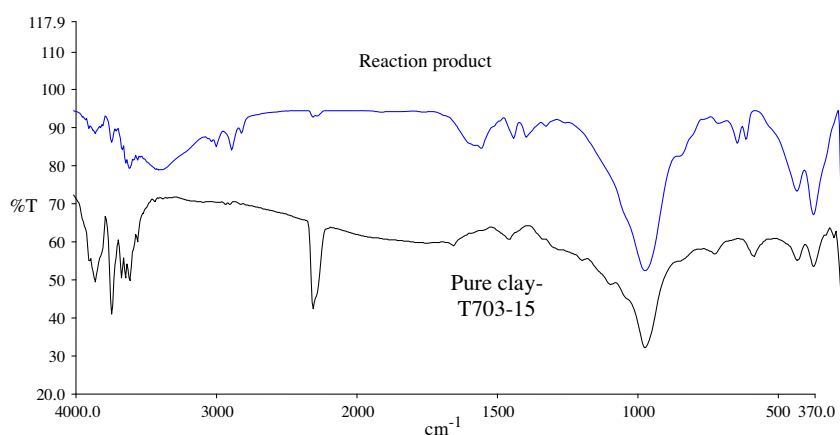


Figure 5. FTIR spectra of clay catalyzed reaction products and pure clay T703–15.

In FTIR spectra of pristine clay and sol–gel material of Cu (II) clay as shown in figure 6, a broad peak at around 3700–3200 cm^{-1} , which is due to Si–OH stretch peak is observed thus indicating loss of water molecules. Si–O–Si asymmetric stretch at 1043.64 cm^{-1} is reduced and Si–O–Si bend peak at 450 cm^{-1} is lost thus confirming the formation of some new material. It can be said that sol–gel material may have been formed.

3.3 XRD analysis

The d -spacing observed for virgin MMT is 1.6 nm ($2\theta = 5.44 \text{ \AA}$) which always increases upon organic modification

(Jash and Wilkie 2005; Stadtmueller *et al* 2005). The d -spacing of various clay catalysts employed in Friedel–Craft alkylation reaction are shown in table 1. It is clear that d -spacing is greatest in acid Pt (II) clay indicating partially exfoliated structure. It can thus be said that better the dispersion of clay platelets, better is the performance of the catalyst.

3.4 Determination of charge properties of catalysts

The ionic character of clay catalyst samples employed in Friedel–Craft alkylation reaction was determined by measuring their Zeta potentials. Zeta potential and pH of all clay

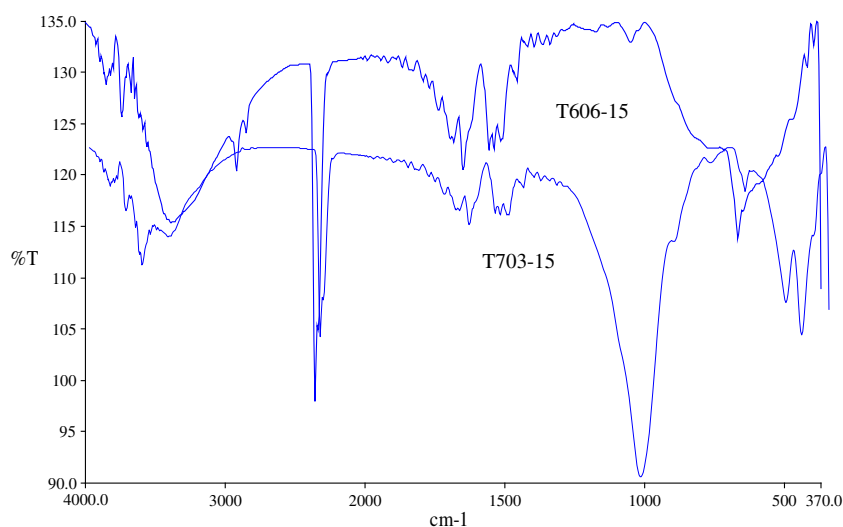


Figure 6. FTIR spectra of sol-gel material of Cu (II) clay (T606-15) and pure clay (T703-15).

Table 1. Table showing *d*-spacing of various clay catalyst samples.

Sl. No	Sample name	<i>d</i> -spacing (nm)	Angle, 2θ
1.	Pure MMT (T703-15)	1.6	5.44
2.	Acid Pt (II) clay (T704-1)	3.6	2.41
3.	Pt (II) clay dispersed by natural dispersant (T704-2)	3.21	2.74
4.	CTAB dispersed Pt (II) clay (T704-3)	3.2	2.75
5.	Sol-gel hybrid of Cu (II) clay (T606-15)	2.9	3.03

catalysts were recorded and shown in table 2. Acid Pt (II) clay has the highest value of zeta potential. The decrease in the trend of the values from acid Pt (II) clay to sol-gel material of Cu (II) clay has been assigned to the compression in the double layer because of higher concentration of ions in bulk.

3.5 Kinetic parameter analysis

Not all collisions between molecules result in a reaction. The molecules must have enough energy for the reaction to occur. The minimum energy that is needed is called activation energy. Catalysts are substances that lower the activation energy and thereby increase the rate of reaction. We report here activation energies, TOF and reaction rates of various clay catalysts employed for Friedel-Craft alkylation reaction of benzyl chloride with toluene in table 3.

Rate of a batch catalytic reaction is fastest at the very beginning when the reactant concentration is highest and

Table 2. Table showing zeta potential and pH of various clay catalyst samples.

Sl. No	Sample name	Zeta potential (mV)	pH
1.	Acid Pt (II) clay (T704-1)	53.0	5.50
2.	Pt (II) clay (dispersed by natural dispersant) (T704-2)	40.7	5.7
3.	CTAB dispersed Pt (II) clay (T704-3)	35.3	5.85
4.	Pure MMT (T704-15)	25.13	8.5
5.	Sol-gel material of Cu (II) clay (T606-14)	24.8	8.66

generally slows down as the reaction proceeds and ultimately stops when all the reactant is used up. TOF will, therefore, vary throughout the course of a batch reaction. Here, in this work, we have reported the initial TOF. Initial TOF is the initial part of a catalytic reaction where rate is fastest and essentially linear. Turnover frequency or turnover rate is determined by taking the number of moles of product formed, dividing that by the number of moles of catalyst used in the reaction, finally dividing this number by time to produce the given amount of product. Its unit is time^{-1} . Acid Pt (II) clay proves to be the best catalyst among all catalysts screened with activation energy as low as 133 kJ/mol and TOF of 0.5 s^{-1} while sol-gel hybrid materials of Cu (II) clay shows activation energy as high as 1694.79 kJ/mol with decreased catalytic activity.

Table 3. Table showing activation energies, rates of reactions, order of reactions, and TOF of various clay catalyst samples.

Sl. No	Catalyst names	E_a (kJ/mol)	$\ln(K_0)$ (s^{-1})	n	TOF (s^{-1})
1.	T703–15	608.6	181.31	0.85	0.18
2.	T704–4	133	39.94	0.88	0.5
3.	T704–1	133	39.94	0.88	0.5
4.	T704–2	212.2	66.97	1.03	0.45
5.	T704–3	308.75	94.36	1.03	0.3
6.	T606–11	555.65	180.9	1.12	0.2
7.	T606–12	509.2	167.92	1.2	0.25
8.	T606–14	1673.19	500.64	1.49	0.15
9.	T606–15	1694.79	519.82	0.82	0.13

4. Conclusions

In conclusion we have established that acidity and dispersion of solid catalyst are two important factors which influence reaction rates and activation energies of a chemical reaction. Among the catalysts used, acid Pt (II) clay and Pt (II) clay dispersed by natural dispersant are shown to be more effective catalysts due to more number of acidic sites and better dispersion of clay platelets. The major advantage of clay as solid catalysts is its good activity as well as its easy removal from the reaction mixture. Moreover, the catalysts are environmental friendly as they prevent hazardous wastes from environment.

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