

Alkylation of aniline with methyl-*tert*-butyl ether (MTBE) and *tert*-butanol over solid acids: product distribution and kinetics

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Abstract

tert-Butylanilines are used in pharmaceuticals, pesticides, plastics, additives and dyes. They are usually prepared by reacting aniline in presence of liquid acid catalysts with pure isobutylene or C₄ fraction from naphtha crackers containing isobutylene. These processes suffer from problems of use of highly corrosive liquid acids and also the source of isobutylene. Both *C*- and *N*-alkylation are possible in the case of aniline depending on reaction conditions such as temperature, source of isobutylene and type of catalyst. In the current study, several solid acids, majority of which were heteropolyacids (HPAs) supported on different clays, were evaluated with both methyl *tert*-butyl ether (MTBE) and *tert*-butanol as alkylating agents in a pressure reactor under autogenous pressure.

Twenty percent (w/w) dodecatungstophosphoric acid/K10 montmorillonite clay (DTP/K10) was found to be the most active for alkylation of aniline with both MTBE and *tert*-butanol. Only *C*-alkylated products were obtained. The yield of mono-alkylated products was over 84% with a selectivity of 53% to 2-*tert*-butylaniline with MTBE at 175 °C. With *tert*-butanol only the mono-alkylated products are obtained at 150 °C with equal isomer distribution. Effects of various parameters on rates and selectivities are discussed. In the presence of DTP/K10, only *C*-alkylated products were obtained. A reaction mechanism is also described with a kinetic model.

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Keywords: Aniline; Alkylation; *tert*-Butylation; MTBE; *tert*-Butanol; Montmorillonite clay; Heteropolyacids; Dodecatungstophosphoric acid; K10 clay; Zinc chloride supported on clay; Sulphated zirconia; Exchanged clay; Kinetics; 2-*tert*-Butylaniline; 4-*tert*-Butylaniline; 2,4-di-*tert*-Butylaniline; Selectivity

1. Introduction

Aniline is used as a building block for the manufacture of several products in chemical and allied industries. Ring alkylated aromatic amines have a variety of uses in chemical synthesis. Some of the early

uses were intermediates for substituted isocyanates, herbicidal compositions, dyestuffs and textile auxiliary agents. More recently aromatic amines have been utilized as chain lengthening or cross-linking components in polyurethane systems. These are commonly referred to as chain extenders. Friedel–Crafts alkylation of aromatic substrates is typically conducted by using highly corrosive homogeneous Lewis acids such as AlCl₃, AlBr₃, ZnCl₂, FeCl₃, TiCl₄ and strong Brønsted acids like sulphuric acid and phosphoric acid using a variety of alkylating agents

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[1]. These acids cannot be reused and cause severe corrosion of equipment as well as effluent treatment problems. A variety of ring or side-chain alkylated products (such as mono-, di-, tri-, *C*-, *N*-, *O*-, or *S*-alkyl) are likely to form depending not only on the nature and position of the functional groups in the parent amine but also on the reactions conditions such as type of catalyst, temperature, pressure, mole ratio, etc. causing separation problems [2–11]. Thus, alkylation of aniline with solid acids has a great industrial relevance from the green chemistry viewpoint [12,13].

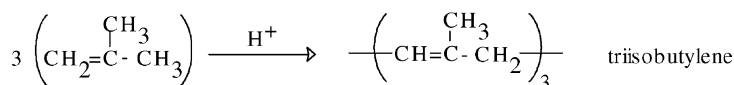
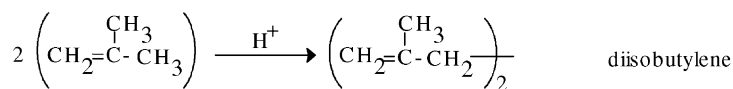
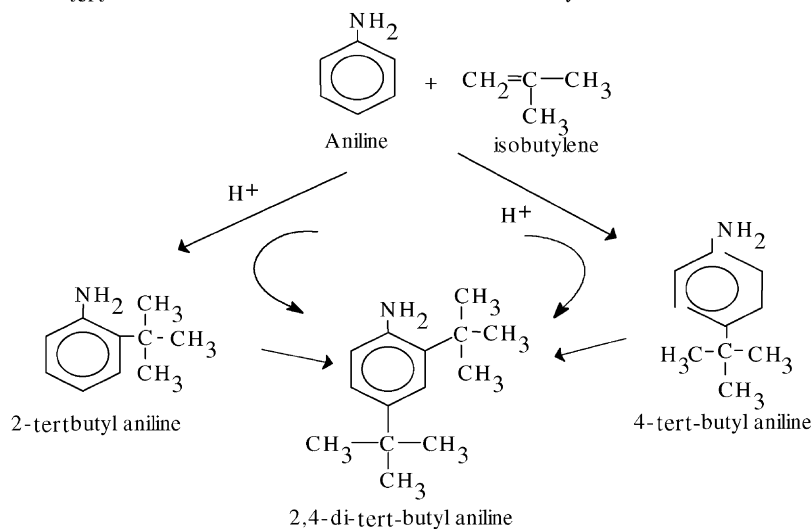
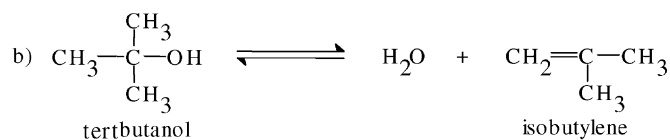
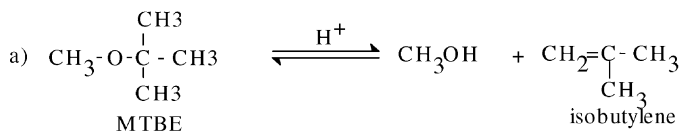
Among alkylated anilines, *tert*-butylanilines are used in pharmaceuticals, pesticides, plastics, additives and dyes. They are usually prepared by reacting aniline in presence of liquid acid catalysts with pure isobutylene or C_4 fraction from naphtha crackers containing isobutylene. Alkylation of aniline is an acid catalysed consecutive reaction with formation of *N*-alkylaniline in the first step which gets further dialkylated to di-alkylaniline under suitable conditions. If olefins are used as alkylating agents, then the oligomerisation of olefins is also possible, making the overall reaction a complex network. These processes are fraught with problems of using highly corrosive liquid acids and also the source of isobutylene. The Friedel–Crafts reaction has long been known as an important way of introducing alkyl groups into aromatic nuclei, and $AlCl_3$ is the most widely used catalyst for the alkylation of aniline [9,10]. The first reports of acid catalysed alkylation of aniline with olefin described the chemistry, with high preference for *para*-substituted product [2–4]. Aniline is readily converted into secondary and tertiary amines by reacting with primary alcohol at 150–180 °C in the presence of catalytic amount (1 mol% based on aniline) of a ruthenium complex such as dichlorotris(triphenyl phosphine) ruthenium. Secondary amines were obtained in excellent yields when aniline was reacted with an equimolar amount of alcohols. With excess quantity of alcohol, tertiary amines were obtained predominantly [11]. Liquid acids are being replaced with solid acids and a variety of zeolitic and non-zeolitic catalysts are being evaluated. *N*-*tert*-butylaniline was prepared in high selectivity under a carefully controlled reaction between aniline and isobutylene at 150 °C in the presence of Al_2O_3/SiO_2 as a catalyst at 42% conversion of aniline with a selectivity of 87%

to the mono-alkylated product [12]. Alkylation of aniline with isobutylene at 130 °C over H-Y zeolite led to both *N*-*tert*-butylaniline and 2-*tert*-butylaniline in 50% yield. With an increase in temperature to 150 °C, the conversion of aniline as well as the selectivity to 2-*tert*-butylaniline was found to increase drastically [13]. Modified zeolites and other metal oxides such as alumina, silica-alumina, iron oxide have been used to get alkylanilines (C_1 – C_6 , cyclohexyl) [14–31]. Patents have been claimed to selectively get *o*-alkyl [14–17], *p*-alkyl [18] and *N*-alkylanilines [19]. The rearrangement of *N*-alkylanilines with the corresponding olefins to *ortho*-alkylated anilines is carried out over modified H-Y and γ -alumina catalysts [17]. AEL type molecular sieves [26] have been used with alcohol as alkylating agent including dimethyl carbonate [27,28]. Other solid acid catalysts such as multimetallic catalysts have also been used [32,33] (Scheme 1).

Over most of the catalysts, it has been found that *C*- versus *N*-alkylation and/or mono- versus di-alkylation are highly temperature sensitive and the pore size and nature of acidic sites play very major roles. With increase in temperature conversion towards di-alkylated product increases [29–31]. At high conversion, *N,N*-di-alkylaniline is formed at the expense of *N*-alkylaniline [29]. At still higher temperatures, *N,N*-di-alkylaniline is found to undergo isomerisation to give *C*-alkylated product [30]. Stronger acidic sites catalyse *C*-alkylation, whereas, *N*-alkylated product of aniline forms with increase in the basic nature of catalyst [7,14,31]. The literature also suggests that exclusive production of ring alkylated products is possible and the *o/p* ratio can be varied using different reactions conditions, alkylating agents and reactor configurations. No kinetic information is available on the heterogeneously catalysed alkylation reactions of aniline.

Due to the problems associated with unavailability, transportation and handling of isobutylene, particularly for usage in low-tonnage fine chemical and speciality manufacture to make *tert*-butyl derivatives, it is advantageous to generate isobutylene in situ, amongst which cracking of methyl *tert*-butyl ether (MTBE) and dehydration of *tert*-butanol are attractive. *tert*-Butanol is typically available as a by-product in the ARCO process for propylene oxide. The cracking of MTBE for the generation of isobutylene has been discussed

Source of isobutylene (in-situ generated)



Scheme 1. Acid catalysed alkylation of aniline with isobutylene generated in situ: product distribution.

[34–36]. MTBE is a good source for the generation of pure isobutylene and the co-product, methanol, can be recovered and reused. On the contrary, the dehydration of *tert*-butanol in situ leads to water as a co-product in the alkylation reaction and thus different yields of the alkylated product are expected vis-à-vis MTBE as an alkylating agent [37–40]. In our laboratory, heteropolyacids (HPAs) supported on clays were

found to be novel catalysts [41] which exhibited superior activity as catalyst in comparison with other solid acids in the alkylation and etherification reactions involving isobutylene in our laboratory [37–43].

This work was undertaken to study the alkylation of aniline with MTBE as well as *tert*-butanol as alkylating agents over solid acids as catalysts including the clay supported catalysts. The reaction kinetics and

mechanism are also discussed with reference to the most active catalyst.

2. Experimental

2.1. Chemicals and catalysts

MTBE was obtained from Texas Petrochemicals Corp., USA. Aniline and *tert*-butanol were obtained from M/s s.d. Fine Chemicals Pvt. Ltd., Mumbai, India. 2-*tert*-Butylaniline (2-TBA), 4-*tert*-butylaniline (4-TBA), 2,4 di-*tert*-butylaniline (2,4-DTBA), *N*-*tert*-butylaniline (NTBA) and *N,N*-di-*tert*-butylaniline (NNDTBA) were obtained from Aldrich. K10 montmorillonite clay was obtained from Fluka, Germany. Filtrol-24, an acid treated clay, was obtained from Engelhard. All other chemicals were of AR grade obtained from reputed firms and used without further purification. Dodecatungstophosphoric acid (DTP), dodecatungstosilicic acid (DTS), dodecamolybdophosphoric acid (DMP) were obtained from s.d. Fine Chemicals Pvt. Ltd., Mumbai, India.

The following catalysts were prepared by well-developed procedures and were characterised in the laboratory: 20% (w/w) heteropolyacids (DTP, DTS and DMP) supported on K-10 clay, Al pillared clay, 20% DTP/silica, 10% AlCl₃ + 10% FeCl₃/K10, Cr-exchanged K10, Zr-exchanged K10 and 20% DTP/activated carbon [42,43], sulphated zirconia [44,45].

2.2. Apparatus and procedure

All experiments were carried out in a 100 ml stainless steel Parr autoclave. A four bladed-pitched turbine impeller was used for agitation. The temperature was maintained at ± 1 °C of the desired value.

Predetermined quantities of reactants and the catalyst were charged into the autoclave, the temperature raised to the desired value and agitation started. Then an initial sample was withdrawn. Further samples were drawn at periodic intervals to generate concentration profiles.

The standard experimental conditions were: 0.1 mol aniline, 0.4 mol MTBE, a catalyst loading of 0.05 g/cm³, 175 °C and 1000 rpm. When *tert*-butanol was used as the alkylating agent, the temperature of

reaction was maintained at 150 °C under otherwise similar conditions.

2.3. Analysis

The products were identified by gas chromatography, mass spectroscopy and IR. A gas chromatograph (Perkin-Elmer Model 8500) was used for routine analysis having a 2 m × 3 mm stainless steel column packed with 10% OV 17/chromosorb WHP and a flame ionisation detector. Calibration curves were prepared by using standard samples and synthetic mixtures and the data were quantified.

3. Results and discussions

3.1. Efficacies of various catalysts

Both MTBE and *tert*-butanol were used as the alkylating agents using a variety of catalysts in the absence of both external mass transfer resistance and intra-particle diffusion limitation. After the preliminary experiments were done, it was found that DTP/K10 was the most active catalyst which was used to assess the influence of external mass transfer on the reaction rate. The speed of agitation was changed from 400 to 1000 rpm under otherwise similar conditions with MTBE. It was observed that the conversion of aniline increased when speed was increased from 400 to 800 rpm, beyond which it was unaffected. Between 800 and 1000 rpm the conversion of aniline remained the same, which suggested the absence of external mass transfer effects. Hence, further reactions were carried out at 1000 rpm. The comparison of activity of different catalysts, which was made at 1000 rpm, was also free from external mass transfer effects for which Wiesz–Prater criterion was used [39,40].

In all 13 different catalysts were employed to conduct the alkylation of aniline with MTBE (Table 1) and some of them were also used with *tert*-butanol (Table 2). Only the ring substitution was found to take place giving 2- and 4-TBA as the major mono-alkylated products with a minor 2,4-DTBA with MTBE. Under the experimental conditions employed in this study, there was no detectable formation of *N*-*tert*-butylaniline or *N,N*-di-*tert*-butylaniline. Analysis was done by using the pure *N*-alkylated

Table 1
Efficacies of different catalysts in alkylation of aniline with MTBE

No.	Catalyst	Activity $\times 10^6$ (mol/(g cat s))	Percentage conversion of aniline	Percentage product selectivity		
				2-TBA	4-TBA	2,4-DTBA
1	20% (w/w) DTP/K-10 clay	3.506	70	53	31	16
2	20% (w/w) DTP/KSF clay	2.717	56	56	32	12
3	20% (w/w) DTP/Filtrol-24 clay	2.630	51	54	28	18
4	20% (w/w) DTP/SWy2 clay	2.410	47	53	36	11
5	DTP	2.586	52	63	29	8
6	K-10 clay	1.972	40	44	37	19
7	KSF clay	1.314	24	45	45	10
8	Filtrol-24 clay	1.840	35	43	41	16
9	20% (w/w) DTS/K10	2.717	56	58	34	8
10	DTS	2.454	48	60	31	9
11	10% AlCl ₃ + 10% FeCl ₃ /K10	2.016	41	54	36	10
12	Al pillared clay	1.884	37	67	26	7
13	S-ZrO ₂	1.402	26	53	36	11

Conditions: Aniline:MTBE, 1:4 mol; catalyst loading, 0.05 g/cm³; temperature, 175 °C; time, 4 h; speed, 1000 rpm; autogenous pressure, 350 psig; autoclave, 100 ml; DTP, dodecatungstophosphoric acid; DTS, dodecatungstosilicic acid; TBA, *tert*-butylaniline; DTBA, di-*tert*-butylaniline.

anilines as well as synthetic mixtures and also by dosing the samples with pure products to find that no *N*-alkylated products were formed. A few material balance studies were done to notice that there were no *N*-substituted products. The maximum conversion achieved with MTBE was only 70% (Table 1) and with *tert*-butanol was 34% with DTP/K10 (Table 2) in 4 h. Further experiments on rearrangement of *N-tert*-butylaniline to the ring alkylated products with MTBE and *tert*-butanol with 20% DTP/K10 catalyst, under similar reactions conditions, showed complete conversion to the ring products.

3.1.1. Product distribution and selectivity

It is worthwhile to examine the selectivity of ring alkylated products in this study. A few patents have been devoted to the exclusive production of *N*-, *ortho*- or *para*-alkylanilines using different homogeneous [7,8] and heterogeneous catalysts [14–19]. Of course, these catalysts are different from the ones used in this study. The product distribution is strongly dependent on the type of alkylating agent or olefin, reaction time, acid strength and type of acidity (Lewis or Brønsted), amount of catalyst, temperature and pressure. There are two major reactions in the alkylation

Table 2
Efficacies of different catalysts in alkylation of aniline with *tert*-butanol

No.	Catalyst	Activity $\times 10^6$ (mol/(g cat s))	Percentage conversion of aniline	Percentage product selectivity	
				2-TBA	4-TBA
1	20% (w/w) DTP/K-10	2.823	34	50	50
2	20% (w/w)/DTP/Filtrol-24	2.781	31	64	36
3	DTP	2.690	31	61	39
4	DTS	2.093	28	57	43
5	K-10	1.508	19	58	42
6	Filtrol-24	1.850	22	50	50
7	KSF	1.763	21	58	42
8	Al pillared clay	1.789	21	66	34
9	S-ZrO ₂	1.081	14	51	49

Conditions: Aniline:*tert*-butanol, 1:4 mol; temperature, 150 °C; catalyst loading, 0.05 g/cm³; speed, 1000 rpm; time, 4 h; autogenous pressure, 200 psig; autoclave, 100 ml.

of aromatic amines, namely, *N*- and *C*-alkylations in the benzene ring. The rearrangement of *N*-alkyl group to ring alkylation is highly temperature sensitive and proportional to the acid strength [17].

The formation of *N*-alkylated products occurs on weak acidic sites and also at lower temperatures [12,23]. These *N*-alkylated products are the most thermodynamically unstable of the three alkylated isomers among 2-, 4- and *N*-alkyl products. Amongst the stability of various *N*-alkylanilines, the following observations have been made. The stability increases in the following order:

p-Alkylaniline (most stable)

> *o*-alkylaniline > *N*-alkyl aniline (least stable)

Amongst the stability of various *N*-alkylanilines at a given temperature, the chain length and structure of the alkyl groups influence the stability as follows:

N-methyl (most stable) > *N*-ethyl \gg *N*-isopropyl

> *N*-butyl \gg *N*-*tert*-butyl (least stable).

The rearrangement of *N*-alkylanilines to ring alkyl anilines has been studied under both homogeneous Lewis acid catalysts and Brönsted acids [5,6], as well as under solid acids such as γ -alumina and H-Y zeolite [17]. The rearrangement of *N*-alkylaniline into the ring alkylated products happens according to the so called Reilly–Hickenbottom mechanism [2–4] modified by Hart–Kosak [5,6]. Reilly and Hickenbottom reported that nuclear alkylation of amines could be effected by heating an *N*-alkylaniline with a homogeneous Lewis acid such as zinc chloride in liquid phase. *N*-*tert*-butylaniline immediately gets converted into the ring products. Exclusive production of ring substituted *tert*-butylanilines has been claimed with Lewis acids such as AlCl₃, AlBr₃, ZnCl₂, FeCl₃, TiCl₄ and strong Brönsted acids like sulphuric acid and phosphoric acid using olefins such as ethylene, propylene, isobutylene, etc [7]. These acids are very strong acids.

The mechanism of formation of *o*-alkylated aniline is because of Brönsted acidity and, whereas, that of *p*-alkylated aniline is due to the Lewis acids [5,6]. The *ortho*-alkylated product is formed due to the reaction between the carbenium ion of the alkylating agent, which is on the surface of the catalyst, and the adsorbed aniline on the adjacent site. The aniline site

may be a Lewis or Brönsted site. It is likely that only Brönsted sites may lead to *o*-alkylated product. This hypothesis was verified by conducting independently a preliminary experiment using *tert*-butanol in presence of Indion-130 a cation exchange resin which contains only Brönsted sites. *o*-*tert*-Butylaniline and trimer of isobutylene were produced. There was no *para* selectivity.

On the contrary when there is a distribution of sites, the *ortho* to *para* ratio will depend on the relative distribution and accessibility of the Lewis and Brönsted sites and the operating temperature and time of contact since *p*-alkylanilines are thermodynamically more stable. *o*-Alkylaniline gets isomerized readily to *p*-alkylaniline at higher temperature to a thermodynamic mixture in homogeneous catalysis and the ratio depends on the pore size distribution and the bulkiness of the alkyl group in heterogeneous catalysis.

The rearrangement of *N*-alkylanilines to ring substituted anilines occurs very easily in the presence of the respective olefin. The reaction occurs with increasing ease as substitution of the double bond increases. The rates are much greater in the presence of isobutylene than propylene which in turn are greater than ethylene. The minimum temperature required to attain the rearrangement decreases substantially as the number of carbon atoms increase in the olefin. For instance,

200 °C for ethylene

> 100 °C for propylene > 50 °C for isobutylene

and the maximum temperature for rearrangement to avoid de-alkylation is:

425 °C for ethylene

> 375 °C for propylene > 250 °C for isobutylene

High temperature leads to the formation of *p*-alkyl anilines. The catalysts were γ -alumina, silica-alumina, or H-Y zeolite [17,18]. Stronger acids such as H-Y zeolites offer greater selectivity to ring substituted products than alumina-silica [15]. In the alkylation of aromatic amines, the molar ratio of olefin to aromatic amine influences the selectivity of the reaction. The use of higher mole ratio of olefin to aromatic amine tends to increase the amount of *ortho*-alkylated product [14,16]. Further, these *N*-alkylanilines undergo

easy rearrangement to *o*-alkyl and *p*-alkylanilines as the acidity and pore size of the catalyst is increased.

3.1.2. Selectivity of different catalysts with MTBE as alkylating agent

Now, it is worthwhile to make a reference to the selectivities of the catalysts used in this study. All catalysts used here are stronger acids than zeolites and have a much broader pore size distribution. The catalysts used in the current studies were all non-zeolitic, strong solid acids including super-acidic sulphated zirconia. Therefore, only *ortho* and *para-tert*-butylated and di-alkylated products were obtained. The entries in Table 1 are arranged to suggest the synergism between the heteropolyacid (HPA) and clay. In all the cases, 20% (w/w) loading of heteropolyacid (HPA) over clay was found to be better than either the clay alone or the HPA alone on unit weight basis.

When 20% DTP was supported on K10, 70% conversion of aniline was obtained with 84% yield of the mono-alkylated products having 53% selectivity of 2-*tert*-butylaniline. There was no formation of oligomers of isobutylene. Whereas, in the case of similarly prepared 20% (w/w) DTS/K10 the conversion of aniline was 56% with a selectivity of 58% to 2-*tert*-butylaniline. DTP and DTS when employed as such without any support gave 52 and 48% conversion of aniline, respectively. Entries 1–6 show that 20% (w/w)/ DTP/K-10 was the most active catalyst and K-10 was the best support. Among the clays (entries 6–8), which are all acid treated, K-10 was the best. The surface areas of the clays and supported clays were measured by N₂-BET method. K-10 has the largest surface area (230 m²/g). However, after loading 20% DTP on K-10 its surface had dropped down to almost half to 107 m²/g. It would mean some of the pores were inaccessible to N₂ molecules during the measurement. The DTP molecules could have occupied a few small junctions making some of the networks of pores totally inaccessible. The uniform deposition of DTP on the walls of the clay had also reduced its size since the formation of the bulkier 2,4-DBA had reduced from 19% at 41% conversion of aniline with K-10 alone to 16% at 70% conversion on 20% DTP/K-10 (entries 6 and 1, respectively). The SEM pictures had indeed shown it as was reported by us in an earlier publication [42].

DTP is a little better catalyst than DTS when taken alone (entries 5 and 10) and in supported form it is far better. In the case of 20% DTS/K-10, there was a further reduction in the surface area of 81 m²/g. These heteropolyacids differ from each other in the sense that in the case of DTP the hetero atom is phosphoric acid, whereas, in case of latter the hetero atom is silicic acid. By the Hammett function scale, DTP is more acidic than DTS. When supported on clay both the HPAs led to higher conversion of aniline in comparison with the unsupported HPAs or the clay support on weight basis. It should be recognised that the supported catalyst contained only 20% HPA and, hence this activity was far significant with respect to the 100% HPA in unsupported form. Thus, there is not only an increase in acidity per unit mass but also a favourable distribution of acidity as Lewis and Brønsted acids. The selectivity to 2-*tert*-butylaniline (2-TBA) was more than 4-*tert*-butylaniline (4-TBA). Another interesting catalyst is a mixture of 10% FeCl₃ + 10% AlCl₃ on K-10 but it gave only 41% conversion and was less acidic.

Sulphated zirconia is a super acid vis-à-vis DTP/K-10 and has much wider pore size distribution [45]. However, a conversion of 26% resulted under otherwise similar conditions in 4 h. This is apparently due to the fact that this catalyst leads to higher rates initially leading to the formation of bulkier molecules like 2,4-DTBA which can block some of the critical pore junctions leading to inaccessible pore networks. Hence, the activity was found to be less.

3.1.3. Selectivity of different catalysts *tert*-butanol as alkylating agent

Since *tert*-butanol as alkylating agent leads to formation of water as co-product, it was decided to evaluate some of the catalysts (Table 2). It was made sure that no external resistance to mass transfer existed by keeping the speed at 1000 rpm, as in the case of MTBE reactions. However, the reactions were carried at lower temperature of 150 °C where the formation of oligomers of isobutylene was avoided and the water generated in situ did not have adverse effect. A similar trend was seen as regards the clays and the HPA on clays. There was a 100% yield of the mono-alkylated products in all the cases. This was due to the fact that the reactions were conducted at lower temperature and the conversions were below 35% of aniline. Twenty percent (w/w) DTP/K10 offered the highest

conversion of aniline (34%) with 50% selectivity of both 2- and 4-TBA. No di-*tert*-butylaniline was formed. The rate of reaction with *tert*-butanol was higher than that with MTBE at 150 °C since the generation of isobutylene was limiting. Aluminium pillared clay was found to be active and selective. Selectivity of 66% to 2-TBA was obtained in the presence of this catalyst. This is because the pillared clays being less hydrophilic in nature, become effective acid catalysts where water is a co-product.

3.2. Effect of water addition

It is known that the presence of water in the reaction mixture could have a detrimental effect on the reaction. Water competes very effectively with organic molecules for adsorption at the active sites and also blocks the pores of the catalyst. To study the effect of water on aniline alkylation with MTBE, reactions were carried out at different water content (Table 3). It was observed that with increasing water content, the conversion of aniline had decreased from 70 to 43%. The rate of reaction was higher when no water was present in the reaction mixture as shown in Fig. 1. Although less conversion of aniline was obtained in the presence of water, better selectivity towards 2-TBA (61%) was obtained when water content was 0.4 mol. This can be attributed to the enhancement in Brönsted sites on the catalyst surface, which are responsible for *ortho*-alkylation. Besides, the di-alkylated product

Table 3

Effect of water on alkylation of aniline with MTBE

Moles of water	Percentage conversion of aniline	Percentage product selectivity		
		2-TBA	4-TBA	2,4-DTBA
0	70	53	31	16
0.2	57	57	31	12
0.4	45	61	32	7
0.8	43	59	31	10

Conditions: Aniline:MTBE, 1:4 mol; catalyst, DTP/K10; catalyst loading, 0.05 g/cm³; temperature, 175 °C; speed, 1000 rpm; time, 4 h; autogenous pressure, 350 psig; autoclave, 100 ml.

also had decreased with increasing water content. In the case of *tert*-butanol as alkylating agent, aniline did not produce any di-alkylated product at 150 °C due to the presence of water generated in situ.

Since 20% DTP/K-10 was found to be the best catalyst, effects of various parameters on the rate of reaction and selectivity of *tert*-butylated anilines were studied over that catalyst.

3.3. Effect of catalyst loading

The catalyst loading was varied from 0.01 to 0.1 g/cm³ with MTBE and *tert*-butanol. The product distribution is given in Tables 4 and 5. With an increase in catalyst loading, there was an increase in the rate of reaction. At a catalyst loading of 0.005 g/cm³, the rate of reaction was very low and the conversion

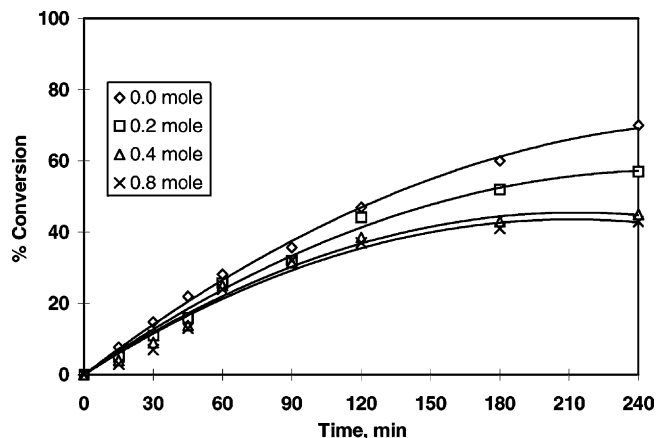


Fig. 1. Effect of water on alkylation of aniline with MTBE: aniline:MTBE, 1:4 mol; temperature, 175 °C; catalyst loading, 0.05 g/cm³; speed, 1000 rpm.

Table 4
Effect of catalyst loading on alkylation of aniline with MTBE

Catalyst loading (g/cm ³)	Percentage conversion of aniline	Percentage product selectivity		
		2-TBA	4-TBA	2,4-DTBA
0.005	13.5	58	42	–
0.01	24	53	45	2
0.025	42	53	34	13
0.05	70	53	31	16
0.10	72	59	26	15

Conditions: Aniline:MTBE, 1:4 mol; catalyst, DTP/K10; temperature, 175 °C; speed, 1000 rpm; time, 4 h; autogenous pressure, 350 psig; autoclave, 100 ml.

Table 5
Effect of catalyst loading on alkylation of aniline with *tert*-butanol

Catalyst loading (g/cm ³)	Percentage conversion of aniline	Percentage product selectivity		
		2-TBA	4-TBA	2, 4- DTBA
0.005	5.2	70	30	–
0.01	8	68	32	–
0.025	19	62	38	–
0.05	34	50	50	–
0.10	41	47	43	10

Conditions: Aniline:*tert*-butanol, 1:4 mol; catalyst, DTP/K-10; temperature, 150 °C; speed, 1000 rpm; time, 4 h; autogenous pressure, 200 psig; autoclave, 100 ml.

of aniline was only 13.5% and no di-*tert*-butylaniline was formed. When the catalyst loading was increased from 0.05 to 0.1 g/cm³, the initial rate of reaction was almost similar and the final conversion was marginally higher (Fig. 2). This could be because of the fact that beyond a certain loading, there existed excess of catalyst sites than actually required by the reactant molecules. Hence, there was a levelling off of the reaction rate. The selectivity to 2-TBA practically remained unchanged with MTBE. However, in the case of *tert*-butanol, it was that the selectivity to 2-TBA decreased with catalyst loading. It appears that the increase in external surface enhances the formation of 2,4-TBA thereby affecting the selectivity to 2-TBA. In the case of *tert*-butanol as alkylating agent, similar observation was made. The initial rate of reaction is plotted against catalyst loading as shown in Fig. 3 for both MTBE and *tert*-butanol to show that the rate is linear in catalyst loading up to 0.05 g/cm³ due to the proportional increase in number of catalytic sites. A theoretical calculation was done based on the Wiesz–Prater criterion to assess the influence of intra-particle diffusion resistance [39,40]. A further proof of the absence of the intra-particle diffusion resistance was obtained through the study of the effect of temperature and it will be discussed later.

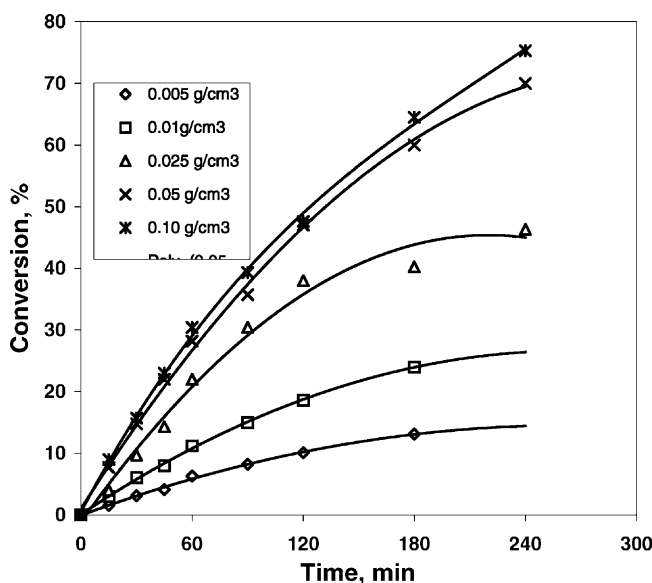


Fig. 2. Effect of catalyst loading on alkylation of aniline with MTBE.

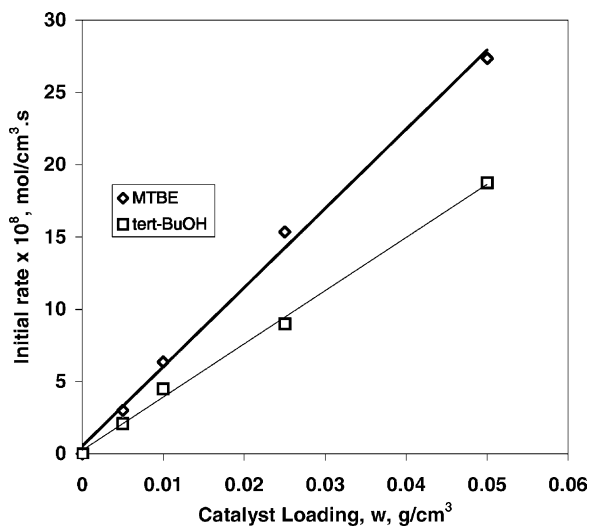


Fig. 3. Effect of catalyst loading on initial rate of aniline.

3.4. Effect of mole ratios of reactants

The product distribution obtained by using different mole ratios of aniline to MTBE is given in Table 6. When aniline to MTBE mole ratio was 1:1, the conversion of aniline was 35% with selectivity to 2- and 4-TBA as 53 and 42%, respectively (Fig. 4). When the

Table 6

Effect of concentration of reactants on alkylation of aniline with MTBE

Aniline:MTBE mole ratio	Percentage conversion of aniline	Percentage product selectivity		
		2-TBA	4-TBA	2,4-DTBA
1:1	35	53	42	5
1:2	52	51	37	12
1:4	70	53	31	16
1:8	73	49	39	12

Conditions: Catalyst, DTP/K10; catalyst loading, 0.05 g/cm³; temperature, 175 °C; speed, 1000 rpm; time, 4 h; autogenous pressure, 350 psig; autoclave, 100 ml.

mole ratio was increased from 1:4 to 1:8, there was an insignificant change in the rate of reaction but the selectivity of 2-TBA was higher (53%) at 1:4 mole ratio than that at 1:8 mole ratio (49%). Similarly the effect of mole ratio of aniline to *tert*-butanol was studied in the range of 1:2 to 1:8, under otherwise similar sets of conditions. The conversion of aniline was only 20% when the mole ratio was 1:2. But selectivities of 2- and 4-TBA were nearly the same in all the experiments (Table 7). No 2,4-DTBA was formed with *tert*-butanol in all experiments. However, it is important to recognise that no di-alkylation was observed with MTBE as well at low temperature and conversion. Dialkylation is strongly temperature dependent.

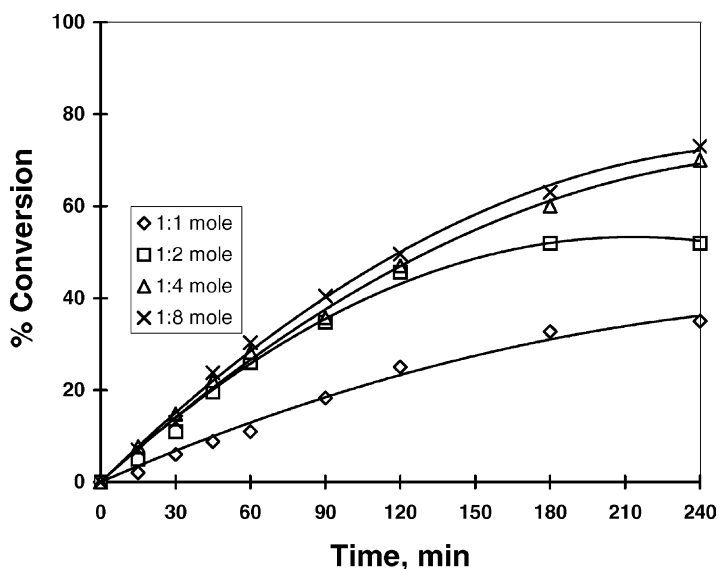


Fig. 4. Effect of mole ratio on alkylation of aniline with MTBE: temperature, 175 °C; catalyst DTP/K10, 0.05 g/cm³; speed, 1000 rpm.

Table 7

Effect of concentration of reactants on alkylation of aniline with *tert*-butanol

Aniline: <i>tert</i> -butanol mole ratio	Percentage conversion of aniline	Percentage product selectivity	
		2-TBA	4-TBA
1:2	20	52	48
1:4	34	50	50
1:8	39	52	48

Conditions: Catalyst, DTP/K-10; catalyst loading, 0.05 g/cm³; temperature, 150 °C; speed, 1000 rpm; time, 4 h; autogenous pressure, 200 psig; autoclave, 100 ml.

Table 8

Effect of temperature on alkylation of aniline with MTBE

Temperature (°C)	Percentage conversion of aniline	Percentage product selectivity		
		2-TBA	4-TBA	2,4-DTBA
155	34	63	37	–
165	47	51	39	10
175	70	53	31	16
185	75	64	33	3

Conditions: Aniline:MTBE, 1:4 mol; catalyst, DTP/K10; catalyst loading, 0.05 g/cm³; speed, 1000 rpm; time, 4 h; autogenous pressure, 350 psig; autoclave, 100 ml.

3.5. Effect of temperature

The effect of temperature on reaction rate was studied in the range from 155 to 185 °C (Table 8). Alkylation of aniline is very much affected by temperature. With an increase in temperature, the rate of reaction increased substantially (Fig. 5). At 155 °C, the rate of reaction was very slow and conversion of aniline was only 27%. At 185 °C, maximum conversion of aniline (75%) was obtained with a selectivity to 2-TBA of 64%. It was noted that at 185 °C, the autogenous pressure in the autoclave was more than 500 psig, indicating very high rates of formation of isobutylene and methanol.

3.6. Reusability of DTP/K10

To investigate the reusability of 20% (w/w) DTP/K10, it was reused three times. After each run, the catalyst was thoroughly washed with hexane and dried in an oven at 120 °C for 4 h. There was practically no loss of acidic centres up to two runs as the conversion of aniline was 70% in both the cases (Table 9) and also no change in selectivity pattern. During the fourth run conversion of aniline decreased to 58%. There is some loss (upto 2%) of the catalyst during filtration and thus there is no loss in catalyst activity on unit weight basis. The catalyst is stable as has been reported earlier for other reactions [37–43].

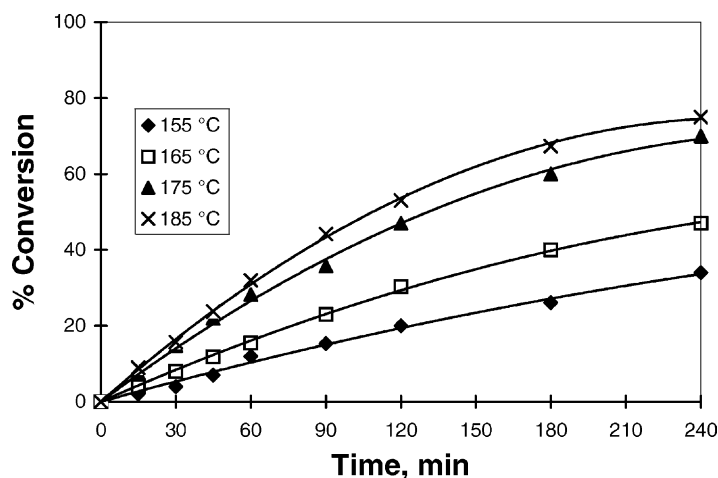


Fig. 5. Effect of temperature on alkylation of aniline with MTBE: aniline:MTBE 1:4 mol; speed, 1000 rpm; catalyst, 20% (w/w) DTP/K10, 0.05 g/cm³.

Table 9
Effect of reusability of DTP/K10 on alkylation of aniline with MTBE

Run no.	Percentage conversion of aniline	Percentage product selectivity		
		2-TBA	4-TBA	2,4-DTBA
1	70	53	31	16
2	68	54	35	11
3	63	58	35	7
4	58	57	35	8

Conditions: Aniline:MTBE, 1:4 mol; catalyst loading, 0.05 g/cm³; temperature, 175 °C; speed, 1000 rpm; time, 4 h; autogenous pressure, 350 psig; autoclave, 100 ml.

3.7. Kinetic model formation

The reaction is assumed to occur by Langmuir–Hinshelwood–Hougen–Watson dual site mechanism. The reaction proceeds through *N*-alkylation. *N*-alkyl derivative is formed first and then it rearranges to the *ortho*-alkylated product. Twenty percent DTP/K10 has both type of sites but more of Brönsted. Aniline is capable of getting adsorbed on Brönsted (S₁) and Lewis (S₂) acid sites, whereas, the alkylating species MTBE or *tert*-butanol (B) gets adsorbed on Brönsted sites. The reaction between A and B adsorbed on Brönsted sites leads to *N*-alkylated product (reaction 1) which is then instantaneously converted into an *ortho*-alkylated product (2-TBA; reaction 2). When A adsorbed on Lewis sites (AS₁) and B adsorbed on Brönsted sites (BS₁) leads to *N*-alkylated product (reaction 3) leads to *para*-alkylated product (4-TBA). This is also the isomerisation of 2- to 4-TBA which is the thermodynamically most favoured product (reaction 4). Further alkylation of both 2- and 4-TBA leads to the di-alkylated product 2,4-DTBA (D; reactions 5 and 6). Initial calculations showed that the overall rate was controlled by the forward surface reaction. Thus, for the sake of brevity, only the relevant equations are presented in what follows.

3.7.1. Surface reactions



where A, aniline; B, MTBE or *tert*-butanol; *N*=*N*-*tert*-butylaniline; *O*, *ortho*-alkylated product; *P*, *para*-alkylated product; D, di-alkylated product; I, isobutylene or MTBE; M, water or methanol; S₁, Brönsted sites; S₂, Lewis sites. Since no *N*-alkylated product was noticed over the conversion range studied, the rate constant k_{R2} is very high leading to only the *ortho* derivative. By considering only the forward reactions, the net rate of reaction of aniline can be arrived at the following:

$$r_A = r_{A1} + r_{A3}$$

$$r_A = \frac{k_{R1} K_{A1} K_{B1} C_A C_B w}{1 + K_{A1} C_A + K_{B1} C_B + K_{N1} C_N + K_{R1} C_R + K_{D1} C_D} + \frac{k_{R3} K_{A2} K_{B1} C_A C_B w}{1 + K_{A2} C_A + K_{P1} C_P + K_{D2} C_D} \quad (8)$$

If there is a weak adsorption of all species, then Eq. (8) is reduced to the following:

$$r_A = (k_O + k_P) C_A C_B w \quad (9)$$

where w is the catalyst loading, g/cm³ and K 's are equilibrium constants.

$$k_O = k_{R1} K_{A1} K_{B1} \quad (10a)$$

$$k_P = k_{R3} K_{A2} K_{B1} \quad (10b)$$

Then since $C_{B0} \gg C_{A0}$, in all standard experiments, it becomes a pseudo-first order reaction, it can be shown

$$-\ln(1 - X_A) = k_{PS} w t \quad (11)$$

where k_{PS} is a pseudo constant.

Inspection of Tables 1–9 shows that the selectivity ratio $S_{2-}/4\text{-TPA}$ in mono-alkylation is almost constant when *tert*-butanol is used as the alkylating agent and also with MTBE at low catalyst loading and temperature. In this mechanism, it is postulated that the distribution of Brönsted to Lewis sites will decide this

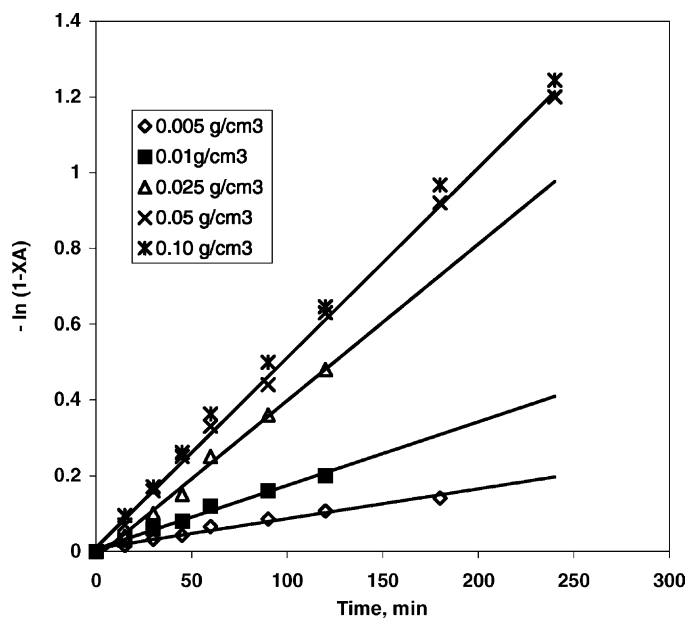


Fig. 6. Plot of $-\ln(1 - X_A)$ vs. time as function of catalyst loading for alkylation of aniline with MTBE.

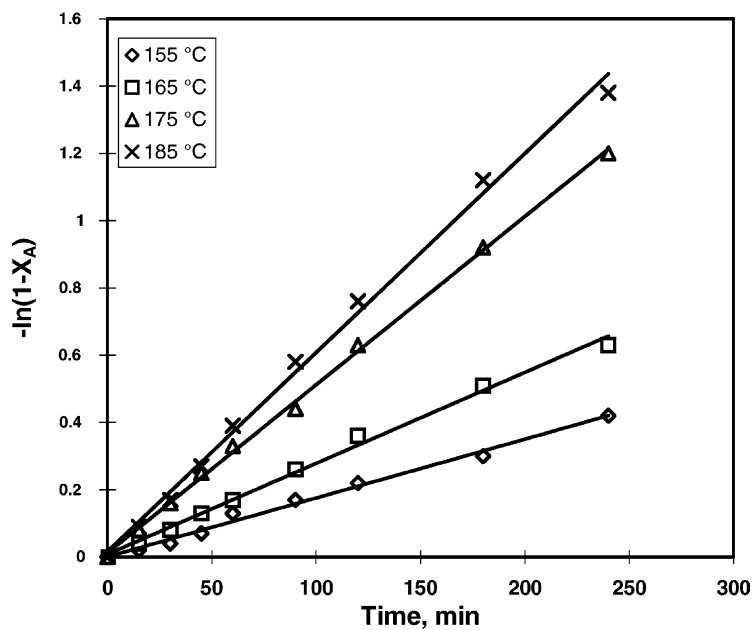


Fig. 7. Plot of $-\ln(1 - X_A)$ vs. time as a function of temperature for alkylation of aniline with MTBE.

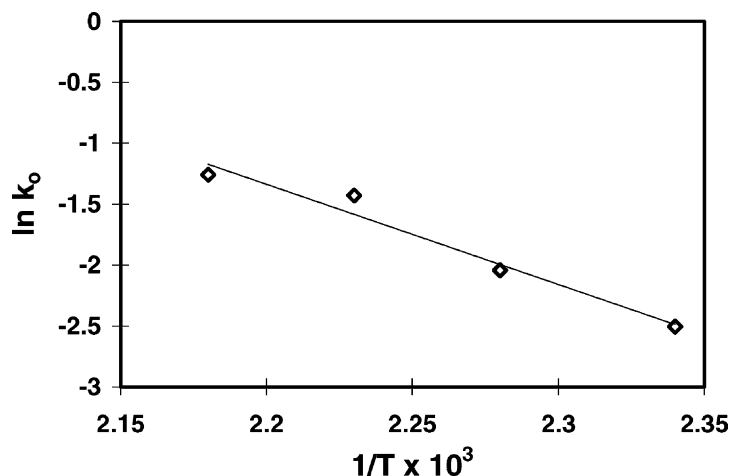


Fig. 8. Arrhenius Plot for alkylation of aniline with MTBE.

ratio. This would suggest that reactions (1) and (3) are prominent and contribute to the overall rate, then the selectivity would be equal to

$$S_{2-/4\text{-TBA}} = \frac{(k_{R1} K_{A1})}{(K_{A2} k_{R3})} \quad (12)$$

If $K_{A1}/K_{A2} \cong 1$, then

$$S_{2-/4\text{-TBA}} = \frac{k_{R1}}{k_{R3}} \quad (13)$$

This ratio will be affected by type of catalyst and temperature. In the case of *tert*-butanol, this is more appropriate since no di-alkylated product is formed. The formation of 2,4-di-*tert*-butylaniline will be both from *o*- and *p*-*tert*-butylanilines when MTBE is used as the alkylating agent.

It is possible to get the pseudo constant from the analysis of the current data. Thus, plots of $-\ln(1 - X_A)$ against t were made for high molar ratios, for each catalyst loading (Fig. 6) and the slope of each line is equal to $k_0 = k_{PS}w$. This is also equivalent to Fig. 2 showing a plot of initial rate against solid loading. Thus, $k_{PS} = 0.1 \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}$ at 175°C was obtained. For different temperature, k_0 values at the same w were calculated from a plot of $-\ln(1 - X_A)$ versus t (Fig. 7). Then the Arrhenius plot of $\ln k_0$ versus $1/T \text{ K}^{-1}$ was made (Fig. 8) to get an apparent activation energy as 16.43 kcal/mol. This value also shows that the reaction is kinetically controlled.

4. Conclusions

The alkylation of aniline was studied using several solid acids based on heteropoly acids, clays, supported clays and sulphated zirconia with both methyl *tert*-butyl ether (MTBE) and *tert*-butanol as alkylating agents in a pressure reactor under autogenous pressure. Twenty percent (w/w) dodecatungstophosphoric acid/K10 montmorillonite clay (DTP/K10) was found to be the most active for alkylation of aniline with both MTBE and *tert*-butanol. Only *C*-alkylated products were obtained. The product distribution is properly explained. The yield of mono-alkylated products was over 84% with a selectivity of 53% to 2-*tert*-butylaniline with MTBE at 175°C . With *tert*-butanol only the mono-alkylated products are obtained at 150°C with equal isomer distribution. Effects of various parameters on rates and selectivities are discussed. A suitable mechanism was developed to analyse the experimental data and kinetic equations were fitted.

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References

- [1] G.A. Olah (Ed.), Friedel–Crafts and Related Reactions, Wiley, New York, vol. I–IV, pp. 163–64.
- [2] P. Reilly, W.J. Hickenbottom, *J. Chem. Soc.* 117 (1920) 103.
- [3] W.J. Hickenbottom, *J. Chem. Soc. Part II* (1932), 2396.
- [4] W.J. Hickenbottom, *J. Chem. Soc. Part II* (1935), 1279.
- [5] H. Hart, J. Kosak, *J. Org. Chem.* 22 (1957) 1752.
- [6] H. Hart, J. Kosak, *J. Org. Chem.* 27 (1962) 116.
- [7] US 3,275,690, 27 September 1966.
- [8] BASF GB 846, 226, 18 December 1958.
- [9] G.G. Ecke, A.J. Kolka, A.H. Filbey, *J. Org. Chem.* 22 (1957) 639.
- [10] R. Stroch, W. Hahn, H. Haberland, *J. Org. Chem.* 69 (1957) 124.
- [11] Y. Watanabe, H. Ige, *J. Org. Chem.* 49 (1984) 3359.
- [12] W.F. Burgoyne Jr., D.D. Dixon, *Chem. Tech.* 11 (1989) 691.
- [13] W.F. Burgoyne Jr., D.D. Dixon, *Appl. Catal.* 62 (1990) 161.
- [14] G.J. Lee, D.D. Rao, G.E. Hartwell, K.D. Anderson, L.N. Moreno, N.N. Shah, US 5,124,483 (23 June 1992).
- [15] W.F. Burgoyne Jr., J.P. Casey, D.D. Dixon, B. Milligan, US 4,745,223 (17 May 1988).
- [16] K. Takahata, K. Taniguchi, US 4,351,958 (28 September 1982).
- [17] W.F. Burgoyne Jr., D.D. Dixon, US 5,001,263, 19 March 1991; US 4,740,620 (26 April 1988).
- [18] A.C. Bayer, C.U. Pittman, L. Wang, E.G. Alley, A.C. Maliyackel, US 5,081,302 (14 January 1992).
- [19] A.C. Bayer, C.U. Pittman, L. Wang, E.G. Alley, A.C. Maliyackel, US 5,030,759 (9 July 1991).
- [20] S. Narayanan, A. Sultana, K. Krishna, *React. Kinet. Catal. Lett.* 52 (1994) 205.
- [21] S. Narayanan, A. Sultana, K. Krishna, *Catal. Lett.* 34 (1995) 129.
- [22] S. Narayanan, A. Sultana, K. Krishna, *Appl. Catal.* 143 (1996) 337.
- [23] P.R.H. Prasad Rao, P. Massiani, D. Barthomeuf, *Stud. Surf. Sci. Catal.* 84 (1994) 1449.
- [24] K.G. Ione, L.V. Malysheva, A.V. Toktarev, in: *Proceedings of the International Symposium on Chemistry of Microporous Crystals*, Elsevier, Tokyo, 1990, p. 319.
- [25] B.L. Su, D. Barthomeuf, *Appl. Catal.* 124 (1993) 73.
- [26] P.S. Singh, B.S. Rao, R. Bandyopadhyay, *Appl. Catal.* 136 (1996) 177.
- [27] Z. Fu, Y. Ono, *Catal. Lett.* 22 (1993) 277.
- [28] P.R.H. Prasad Rao, P. Massiani, D. Barthomeuf, *Catal. Lett.* 31 (1995) 115.
- [29] S. Narayananand, B.P. Prasad, *J. Mol. Catal.* 96 (1995) 57.
- [30] S. Prasad, B.S. Rao, *J. Mol. Catal.* 62 (1990) L17.
- [31] C.N. Pillai, R.B.C. Pillai, *Ind. J. Chem.* 32B (1990) 592.
- [32] M. Rusek, in: *Proceedings of the Ninth International Conference on Catalysis*, Calgary, Canada, vol. 3, 1988, p. 1138.
- [33] R.G. Rice, E.J. Kohn, *J. Am. Chem. Soc.* 77 (1995) 4052.
- [34] F. Cunill, J. Tejero, J.F. Izquierdo, *Appl. Catal.* 34 (1987) 341.
- [35] J. Tajero, F. Cunill, S. Manzano, *Appl. Catal.* 38 (1988) 327.
- [36] J. Tajero, F. Cunill, S. Manzano, *Appl. Catal.* 38 (2) (1998) 327.
- [37] G.D. Yadav, N. Kirthivasan, in: J.P. Blitz, B. Charles (Eds.), *Fundamental and Applied Aspects of Chemically Modified Surfaces*, Little, Royal Society of Chemistry, UK, 1999, pp. 254–269.
- [38] G.D. Yadav, A.A. Pujari, A.V. Joshi, *Green Chem.* 1 (6) (1999) 269.
- [39] G.D. Yadav, N.S. Doshi, *Catal. Today* 60 (2000) 263.
- [40] G.D. Yadav, N.S. Doshi, *Appl. Catal. Part A: Gen.* 236 (2002) 129–147.
- [41] G.D. Yadav, N. Kirthivasan, *J. Chem. Soc., Chem Commun.* (1995) 203.
- [42] G.D. Yadav, V.V. Bokade, *Appl. Catal. Part A: Gen.* 147 (1996) 299.
- [43] G.D. Yadav, N. Kirthivasan, *Appl. Catal. A* 154 (1997) 29.
- [44] P.S. Kumbhar, G.D. Yadav, *Chem. Eng. Sci.* 44 (1989) 2535.
- [45] G.D. Yadav, J.J. Nair, *Micro. Meso. Mater.* 33 (1999) 1.