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Synthesis of Linear Phenyldodecanes by the Alkylation of Benzene with 1-Dodecene over Non-Zeolitic Catalysts

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Abstract:

Linear alkylbenzenes (LAB) are typically manufactured by the alkylation of benzene and α-olefin, employing HF or $AlCl_3$ as catalyst. LAB are the precursors of linear alkylbenzene sulphonates (LABS) used in a variety of industries. Various acid catalysts are being explored by different researchers, and zeolites are claimed to be effective. The isomer distribution depends strongly on the type and nature of the catalyst and reaction conditions. The liquid-phase alkylation of benzene with 1-dodecene was examined by using several non-zeolites based on clays, pillared clays, and clay-supported heteropolyacids such as dodecatungstophosphoric acid (DTP), dodecatungstosilicic acid (DTS), and dodecamolybdophosphoric acid (DMP). The activities and selectivities of K-10 clay, 20% w/w heteropolyacids (DTP, DMP, and DTS) supported on K-10, Filtrol-24, Al pillared clay, 20% w/w DTP/silica,10% $AlCl_3$/10% $FeCl_3$/K-10, DTP, Cr-exchanged K-10, sulphated zirconia, Zr-exchanged K-10, and 20% DTP/activated carbon were evaluated. It was found that 20% w/w DTP/K-10 clay offered the best conversion with favourable product distribution. A molar ratio of 10:1 benzene/1-dodecene favoured the formation of linear dodecylbenzenes (LAB). However, with decreasing benzene concentration, the formation of didodecylbenzenes increased. The best parameters for the alkylation were established. A mechanistic and kinetic model was developed and validated against experimental data. Benzene alkylation was also accomplished with 1-octene, 1-decene, and 1-tetradecene under otherwise similar sets of conditions. It was found that the rate of benzene alkylation decreased with an increase in the chain length of α-olefin.

Introduction

Linear alkylbenzene sulphonates (LABS), containing different carbon atoms in the alkyl chain, are the most important biodegradable surfactants that are used in formulations of light-duty (C11−C12) and heavy-duty (C12−C14) detergents, lubricants (C16−C24), and surfactant flooding (C16) in tertiary oil recovery. LABS are manufactured by sulphonation of linear alkylbenzenes (LAB) which in turn are traditionally synthesised by the Friedel−Crafts alkylation of benzene with α-olefins[1−5] by employing HF or $AlCl_3$ as catalyst or with chloroalkanes by using $AlCl_3$. The final isomer distribution in the product LAB strongly depends on the nature and distribution of acidity (Brønsted or Lewis) and amount of catalyst, solvent, temperature and the position of the double bond in the starting olefin.[6−12] The position of the phenyl group and the alkyl chain length in LABS are important factors in determining their surface active properties and biodegradability.[13,14] Both HF and $AlCl_3$ being homogeneous acid catalysts lead to formation of all 5 isomers from 2- to 6-phenyldodecanes but with varying distribution[8] and these catalysts are a source of pollution and corrosion of reactors and pose disposal problems. Further, its being hazardous and highly corrosive, HF requires special handling and equipment design. Thus there is a tremendous scope to develop ecofriendly, reusable, noncorrosive and cheap catalysts for the alkylation of benzene with α-olefins.

Alkylation of benzene with 1-dodecene was found to yield mainly monoalkylated product with alumina pillared clay as catalyst,[15] whereas silica gel was shown to be superior support for silicotungstic acid (STA) than alumina and silica−alumina and 20% w/w/STA/silica gel led to a conversion of 98% with 90% selectivity to monoalkylated product.[16] Different crystalline aluminosilicates are claimed to be active catalysts for alkylation of aromatics.[17−20.] For instance, alkylation of benzene was effectively carried out with propene, 1-butene and 1-decene over rare earth exchanged X and Y zeolites[21] and with an industrial mixture of higher

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alkenes over β-zeolite, H-mordenite and ZSM-12 in Sivasanker's laboratory[22,23] including a recent report[24] on alkylation of benzene with 1-dodecene on H−USY, HY, H-mordenite, Mg−H-mordenite, Fe−Mg−H-mordenite and H−ZSM-5.

Mixtures of LABS of different chain length are preferred in detergents in order to handle any of several end uses in which a particular formulation may be employed.[10] The effect of carbon chain length and phenyl isomer distribution on the properties of LABS was studied and a comparison made of high and low 2-phenyl LABS homologues[11] to establish that the 2-phenyl content had little effect on LABS performance in both light- and heavy-duty detergent applications, and the carbon number chain size was far more important. However, the biodegradability of 2-phenyl and 3-alkane isomer is higher than the central ones such as 4-, 5- and 6-phenyldodecanes.[13] Some catalysts do not produce 6-isomer at all.[22,25] Baumgartner[14] claimed that optimum detergency power occurs, when the linear alkyl chain contains 11 to 12 carbon atoms. In the case of n-phenyldocanes and their sulphonates, the position of benzene ring in the alkyl chain affects the ease of biodegradability, with external isomers being more readily degraded than the internal ones.[25,26] Thus 2-, 3-, and 4- phenyldodecanes would be preferred for making LABS from biodegradability viewpoint in comparison with the 5- and 6- isomers. The ratio of total concentrations of 2-, 3- and 4- isomers to that of 5- and 6- isomers (with no branched phenyldocanes or didoceylbenzenes) is taken as a yardstick of biodegradability and environmental acceptability[27] and less content of 5- and 6-isomers is beneficial for sulphonation and formulation. The longer the alkyl chain in a LAB the better is the degradation and 2-phenyldodecane is the most biodegradable in all homologues.

From the foregoing it is evident that there is a scope in developing newer catalytic processes for LAB manufacture, particularly since there is no open literature on kinetics and product distribution using non-zeolitic catalysts which may be cheaper. We have reported the novelty and efficacy of clay supported heteropolyacids in a large number of processes, with reference to a variety of industries such as pharmaceuticals and drugs, rubber chemicals, dyestuff, agrochemicals, and perfumery and flavour chemicals.[28−39] Thus the aim of the current research was to evaluate the applicability of a variety of non-zeolitic solid acids, such as clays, pillared clays, clay supported heteropolyacids, and sulphated zirconia with a view to find the most active catalyst and favourable product distribution useful for making LABS. Some of these catalysts can be synthesised more easily and cheaply and have proved to be better than zeolites for liquid-phase reactions. This paper delineates the evaluation of several catalysts including kinetic modelling.

Experimental Section

Chemicals and Catalysts. 1-Dodecene, 1-octene, 1-decene and 1-tetradecene (99% pure) were obtained from Albemarle Corporation, USA. Authentic samples of phenyldodecanes and phenyldidocanes were obtained from Indian Petrochemical Ltd, Baroda, India. Benzene (A. R.), dodecatungstophosphoric acid (DTP), dodecatungstosilicic acid (DTS), dodecamolybdophosphoric acid (DMP) were obtained from s.d. Fine Chemicals Pvt. Ltd, Mumbai, India. K-10 montmorillonite clay was obtained from Fluka, Germany. Filtrol-24 was procured from Engelhard Inc.

The following catalysts were prepared by well-developed procedures and characterised in this laboratory. 20% w/w heteropolyacids (DTP, DTS and DMP) supported on K-10 clay,[28] Al pillared clay,[28] 20% DTP/silica,[30] 10%$AlCl_3$/10% $FeCl_3$/K-10,[28] Cr-exchanged K-10,[28] sulphated zirconia,[29] Zr-exchanged K-10[28] and 20% DTP/activated carbon.[30]

Apparatus and Reaction Procedure. All experiments were conducted in a batch mode by using a 100 mL capacity Parr autoclave. A standard experiment consisted of 0.041 mol of 1-dodecene and 0.41 mol of benzene and a known quantity of catalyst (typically 0.05 g/mL). The autoclave was gradually heated to 150 °C and stirring was then started at 1000 rpm, under autogenous-pressure. Samples were withdrawn at regular intervals starting from initial time and analysed by gas chromatography.

Analysis. A gas chromatograph (Perkin-Elmer Model 8500) with a flame ionisation detector was used with 2m × 0.003 m column, packed with 10% OV 17/chromosorb WHP. Synthetic mixtures were used for calibration and quantification of the collected data. After the catalyst was filtered, products were separated by fractional distillation. Benzene was removed first followed by unreacted 1-dodecene and then alkylbenzenes were distilled out under vacuum. Identification was made through GC-MS as well as by comparison with authentic material.

Results and Discussion

Comparison of Activities of Different Catalysts. Several catalysts were employed to evaluate their efficacy in the alkylation of benzene with 1-dodecene at a mol ratio of 10:1 benzene/1-dodecene. Table 1 lists the efficacy of the various catalysts in order of their activity with the corresponding selectivity to 2- and 3-phenyldodecanes. The K-10 clay-based catalysts were more effective, which included heteropolyacids (DTP, DMP, and DTS) supported on K-10, Filtrol-24 clay, Al-pillared K-10 clay, and K-10 clay itself. Twenty percent

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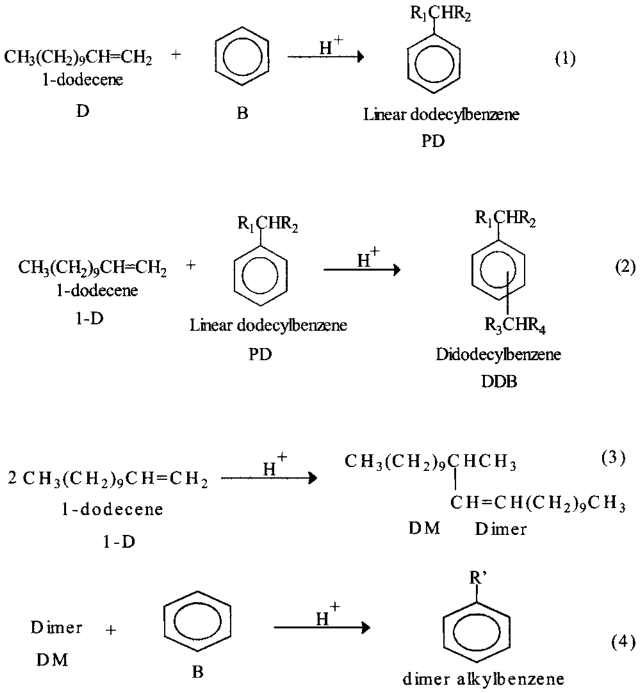
Table 1. **Effect of different catalysts on alkylation of benzene with 1-dodecene[a]**

run	catalyst	conversion of C_{12} %	selectivity of 2-phenyldodecane (%)	selectivity of 3-phenyldodecane (%)
1	20% w/w DTP/K-10	97	32	62
2	20% w/w DMP/K-10	92	28	52
3	20% w/w DTS/K-10	91	29	50
4	Filtrol-24	85	22	47
5	Al pillared clay	80	31	47
6	K-10	71	27	30
7	20% w/w DTP/silica	57	35	42
8	10% w/w$AlCl_3$/ 10% w/w $FeCl_3$/K-10	32	45	20
9	Al-exchanged K-10	22	33	42
10	Cr-exchanged K-10	12	30	41
11	sulphated zirconia	12	30	32
12	Zr-exchanged K-10	10	30	35
13	20% w/w/DTP/carbon	~0	0	0

[a] Conditions: 1-dodecene:benzene, 1:10 mol, temperature 150 °C, catalyst loading: 0.05 g/cm^3, speed: 1000 rpm. Autoclaved. DTP: dodecatungstophosphoric acid. DTS: dodecatungstosilicic acid. DMP: dodecamolybdophosphoric acid.

Scheme 1. **Possible series and parallel reactions during alkylation of benzene with 1- dodecene**



DTP/K-10 was found to be the best with 97% conversion of 1-dodecene, all leading to only the monoalkylated dodecylbenzenes. It is relevant to throw light on product distribution and reaction mechanism. The alkylation of benzene with olefins proceeds through the carbenium ion mechanism (Scheme 1). In the case of 1-dodecene there is a possibility of formation of six carbenium ions of the olefin whose relative stability increases as the C-number increases, the least stable being the 1-phenyldodecane isomer. In fact, due to its being highly unstable, 1-phenyldodecane has not been detected by any researcher for both homogeneous and heterogeneous catalysts, and 2-phenyldodecane is the first stable isomer. Thus, for homogeneous catalysts the thermodynamic isomer distribution would be expected to contain increasing amounts of 2- through 6- isomers, the 2-isomer being the smallest in quantity. This was indeed found by Alul[8] for HF-catalysed homogeneous reaction after thermodynamic equilibrium had been reached. Two reasons were advocated for different product distributions for homogeneous catalysis, by both HF and $AlCl_3$: (i) existence of two equilibrium steps due to isomerisation, one for the olefin and another for the phenyldodecanes and (ii) the difference in the rates of isomerisation of the olefin and the phenyldodecanes. HF catalyses the isomerisation of 1-dodecene into an equilibrium mixture of olefins but does not equilibrate the phenyldodecanes even at 55 °C; on the other hand $AlCl_3$ does so. However, this ratio could be altered by using a suitable catalyst;[16−20] and shape selectivity[22] and the nature of acidity [23,24] have a profound impact on product distribution.

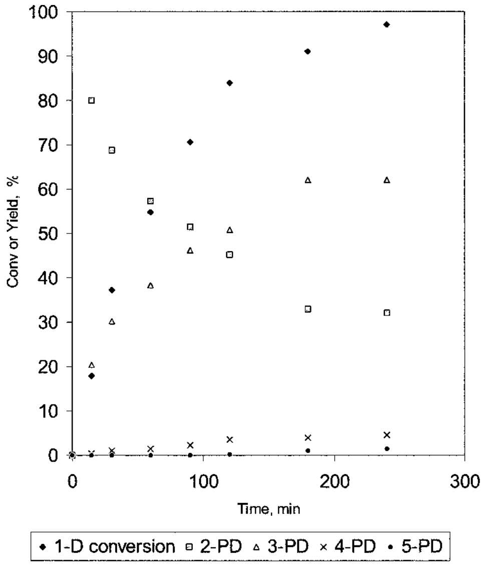


Figure 1. **Alkylation of benzene with 1-dodecene over 20% DTP/K-10. Distribution of linear phenyldodecanes in the reaction mixture. Reaction conditions: benzene:1-dodecene = 10: 1, 150 °C, 1000 rpm, autoclaved. 20% DTP/K-10 catalyst loading: 0.05 g/mL.**

Thus, the secondary carbon atom of the alkyl chain is first attached to benzene, and further products can be formed due to the proton shifts caused by the catalyst (Scheme 1). After monoalkylation, dialkylated product can be formed under a certain set of conditions such as high concentration of olefin in comparison with benzene concentration and reaction temperature. The literature suggested that the amount of dialkylate could be reduced by using a molar excess of benzene over 1-dodecene (above 5:1) and by controlling the temperature and the type of acidity of the catalyst and its loading.

In the current case, at a mol ratio of 10:1 benzene/1-dodecene, over 20% DTP/K-10, the most active catalyst, only four isomers of linear phenyldodecanes were formed with 97% conversion of 1-dodecene with a selectivity of 32% to 2-phenyldodecane and 62% to 3-phenyldocane with minor amounts of 4- and 5-isomers (Figure 1). 6-Phenyldodecane was not detected, and it can be explained as follows. 6-Phenyldocane is bulky molecule[22−24] and tends to block pores of microporous catalysts; with solid acids its formation can be suppressed. With mordenite H-M,[22] Mg-H-M[24] and Fe-H-M,[24] no 6-isomer was formed, and less than 2% of both 4- and 5-phenyldodecanes were formed even at 100%

conversion, whereas H-ZSM-5 was ineffective.[24] Thus, K-10 clay pore structure can be suitably adjusted to get favourable product distribution.

In the current studies, 10 of the 13 catalysts were montmorillonite K-10 clay-based, and another was Filtrol-24 clay. After supporting with the heteropolyacids (HPA), the pore size of K-10 is significantly reduced due to deposition of the Keggin-structured HPA on the accessible pore walls, and they occupy many small-sized pore junctions, thereby reducing the accessibility of some networks.[39] HPAs are more acidic than acid-treated clay. Consequently, the distribution of acidity is also changed significantly among Brønsted and Lewis acid centres, both of which are required for alkylation. Because of this structural change, 20% DTP/K-10 was found to be the most effective catalyst than K-10 in a number of our studies.[28,30,39] The surface areas of the catalysts by nitrogen BET method for K-10 clay and DTP/K-10 were measured as 230 and 107 m^2/g, respectively. Since both the catalysts were pretreated in similar way prior to analysis, the reduction in surface area of DTP/K-10 is due to the blockage of the smaller pores by the active species. Indeed, the pore structure of DTP/K-10 is suitable for formation of smaller isomers (2- and 3-phenyldodecanes), which could get diffused in and out of the pore networks better than higher-numbered ones such as 6-isomers. Thus, there is a shape selectivity, and a greater amount of 3-isomer was formed than of 2-isomer with time. There is a transition-state shape selectivity, and the amounts of 4- and 5- isomers are therefore very low. The bulkiest isomer is therefore was not formed. With K-10 clay as catalyst per se, 71% conversion of 1-dodecene was obtained, all leading to dodecylbenzene isomers with 27% selectivity of 2-phenyldodecane. Other heteropolyacids such as DTS and DMP supported on K-10 also showed better activity than K-10 alone. Exchanged clays such as Al exchanged K-10, Zr exchanged K-10 and Cr exchanged K-10 showed much lower activity. There is a clear synergism between the clay and heteropolyacids which was reported earlier for etherification.[28] Another interesting catalyst is $FeCl_3-AlCl_3$/K-10. It gave 45% selectivity to 2-phenyldodecane, but the conversion was only 32% in 4 h.

How both type of acidity and pore network accessibility affect the product distribution can be explained with DTP/carbon and sulphated zirconia as catalysts. Carbon-based DTP did not give any measurable concentration of any isomers, whereas sulphated zirconia was less effective than 20% DTP/K-10. Sulphated zirconia is a superacid vis-à-vis DTP/K-10 and has a much wider pore-size distribution and thus can lead to higher rates initially, leading to the formation of bulkier molecules such as didodecylbenzenes. However, it was not more active due to the type and distribution of acidity, and indeed there could be some formation of didocylbenzene which could block the accessibility, thereby reducing the acidity. The BET surface area of sulphated zirconia had dropped from 96 to 70 m^2/g at the end of the reaction. When DTP was supported on carbon, there was no conversion of 1-dodecene, perhaps due to strong intraparticle diffusion resistance offered by the bulky molecules and pore blocking. Pores of carbon are narrow slits, and accessibility can be affected drastically when bulky molecules are used.

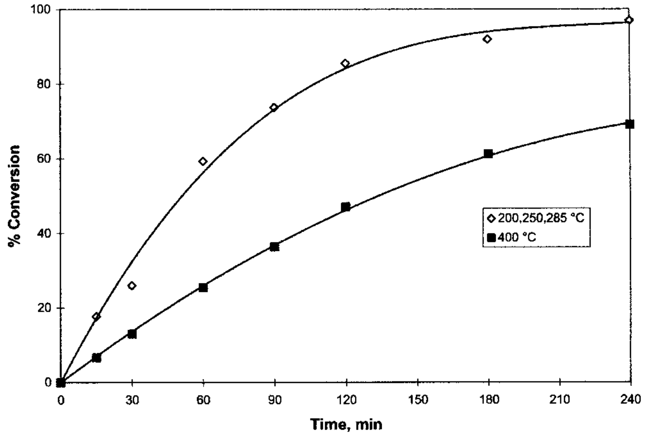


Figure 2. **Effect of calcination temperature on benzene alkylation with 1-dodecene. C_{12}:C_6H_6, 1:10 mol; catalyst DTP/K-10, 0.05 g/mL; temperature, 150 °C; speed, 1000 rpm; reaction time, 4 h.**

Thus, in all further experiments 20% DTP/K-10 was used as the catalyst. The possibilities of formation of some heavier alkylate as byproducts under different conditions particularly when benzene to 1-dodecene ratio was 2:1 are given in Scheme 1 and described below.

1. Dialkylation: It occurs by alkylation of linear dodecylbenzene with a second 1-dodecene molecule (reaction 2). R_1, R_2, R_3 and R_4 are linear alkyl chains. The above depiction of DDB includes different isomers.

2. Oligomerisation of 1-dodecene followed by benzene alkylation (reactions 3 and 4).

It was found that the main products were linear alkylbenzenes whenever the mol ratio of benzene to 1-dodecene was 10:1, and it was used in all experiments in the current investigation. Oligomerization of 1-dodecene itself and the benzene alkylation due to oligomerised 1-dodecene were not at all observed.

Effect of Calcination Temperature. The activity of 20% DTP/K-10 can be a function of temperature because of some water of hydration bound to the catalyst. Hence, the catalyst was calcined at four different temperatures, namely, 200, 250, 285, and 400 °C for 3 h. As shown in Figure 2, the conversion of 1-dodecene remained unchanged up to 285 °C. Conversion to monoalkylated products was 97% with 34% selectivity for 2-phenyldodecane and 62% for 3-phenyldodecane. The conversion to monoalkylated products was reduced to 69% when the catalyst was calcined at 400 °C. It was due to the loss of interlayer water in the clay at high temperature, which had resulted in collapse of interlayer of clay and also due to sintering and decomposition of DTP above 300 °C. Under such circumstances loss of both the effective area of the support and the active sites would occur, resulting in net loss of activity. Independent experiments on the pore-size distribution measurements and XRD as a function of temperature had showed that the pore size gets drastically reduced and that the catalyst activity drops substantially.[39]

Since 20% DTP/K-10 calcined at 285 °C was the best catalyst, the effect of various parameters on the rate of reaction, and hence conversion, was studied under otherwise similar conditions. Characterization of the catalyst is reported earlier by us,[33,34,39] and a brief summary is provided here. As stated earlier, the surface areas of the catalysts by nitrogen BET method for K-10 clay and DTP/K-10 were measured as 230 and 107 m^2/g, respectively. Since both the catalysts were pretreated in similar way prior to analysis, the reduction in surface area of DTP/K-10 is due to the blockage of the smaller pores by the active species. It appears that the active species are held in a few junctions of such dimensions from which the access to smaller pores is denied, thereby leading to the decrease in accessible surface area. The average particle size of both K-10 and DTP/K-10, as determined by image analysis, was in the range of 600 μm. The XRD studies of DTP/K-10 had indicated that in the impregnation process, the clay had lost some of its crystallinity compared to K-10. The cation-exchange capacity (CEC) of the catalysts was determined by the method to observe that DTP/K-10 possesses higher CEC than K-10. This may be due to some additional surface protons, which come by way of heteropolyacid impregnation, which may play a role on account of easy availability for the exchange reaction. We have earlier reported[39] that on the basis of the actual quantity of DTP loaded on the support in comparison with the same unloaded catalyst or the support K-10 alone, the turnover frequency is greater in the case of the supported catalyst. Thus, there is a synergism between DTP and K-10, leading to higher activity. In the case of DTP/K-10 there are lot of dispersed particles on the surface of the support K-10 as revealed by SEM photomicrographs. FTIR studies of K-10 showed that there were Si−O and Si−O−Al linkages and that the OH groups are bonded to the Al atoms, whereas in DTP/K-10 the presence of H_3O^+ (Brønsted acidity) and the linkage of phosphorus was indicated.

Effect of Speed of Agitation. The influence of external mass-transfer resistance was studied for the transfer of the limiting reactant 1-dodecene to the external surface of the catalyst particle at different speeds of agitation at 150 °C for a catalyst loading of 0.05 g/cm^3. The effect of speed of agitation was studied at 250, 700, 800,900, 1000, and 1200 rpm and it was found that the conversion of 1-dodecene had increased from 250 to 700 rpm only marginally. From 700 to 1200 rpm the conversion and product distribution was practically similar in all the cases. Thus, the external resistance to mass transfer was absent beyond 700 rpm. However, to be on safer side and to avoid attrition of the catalyst, further experiments were conducted at 1000 rpm.

Assessment of External and Internal Resistance to Mass Transfer. This is a typical solid−liquid slurry reaction involving the transfer of 1-dodecene (D) and benzene (B) from the bulk liquid phase to the catalyst wherein external mass transfer of reactants to the surface of the catalyst particle, followed by intraparticle diffusion, adsorption, surface reactions and desorption take place. The influence of external solid−liquid mass transfer resistance must be ascertained before a true kinetic model could be developed. Since benzene was always used in excess, there is likelihood of mass transfer resistance to the transfer of 1-dodecene from the bulk liquid phase to the external surface of catalyst particle.

At steady state, the rate of mass transfer (r_D) per unit volume of the liquid phase ($mol{\cdot}cm^{-3}{\cdot}s^{-1}$) is given by:

$$r_D = k_{SL-D}a_p\{[D_0] - [D_s]\} \tag{5}$$

(rate of transfer of D from bulk liquid to external surface of the catalyst particle)

$$= k_{SL-B}a_p\{[B_0] - [B_s]\} \tag{6}$$

(rate of transfer of B from the bulk liquid phase to the external surface of the catalyst particle)

$$= r_{obs} \tag{7}$$

= rate of reaction within the catalyst particle

where, k_{SL} is the solid−liquid mass-transfer coefficient of the concerned species (cm/s), a_p is the external surface area of the particle (cm^2/cm^3 liquid-phase volume), subscript o and s denote the bulk liquid phase and external surface concentrations respectively, in mol/cm^3.

Depending on the relative magnitudes of external resistance to mass transfer and reaction rates, different controlling mechanisms have been put forward.[29] When the external mass-transfer resistance is small, then the following inequality holds,

$$1/r_{obs} \gg \frac{1}{k_{SL-D}a_p[D_0]} \quad \text{and} \quad \frac{1}{k_{SL-B}a_p[B_0]} \tag{8}$$

The observed rate r_{obs} could be given by three types of models wherein the contribution of intraparticle diffusion resistance could be accounted for by incorporating the effectiveness factor η. These models are (a) the power law model if there is very weak adsorption of reactant species, (b) Langmuir−Hinshelwood−Hougen−Watson model, (c) Eley−Rideal model.

It is therefore necessary to study the effects of speed of agitation, catalyst loading, and particle size to ascertain the absence of external and intraparticle resistance so that a true intrinsic kinetic equation could be used.

According to eq 8, it is necessary to calculate the rates of external mass transfer of both 1-dodecene (D) and benzene (B) and compare them with the rate of reaction.

For a typical spherical particle, the particle surface area per unit liquid volume is given by

$$a_P = \frac{6w}{(\rho_P d_P)} \tag{9}$$

where w = catalyst loading g/cm^3 of liquid phase, ρ_p = density of particle g/cm^3, and d_p = particle diameter, cm.

For the maximum catalyst loading used (0.08 g/cm^3) for a particle size (d_p) of 0.06 cm, in the current studies, a_p = 9.41 cm^2/cm^3 liquid phase. The liquid-phase diffusivity values of the reactants D and B, denoted by D_{DB} and D_{BD}, were calculated by using the Wilke-Chang equation[40] at 150 °C as 5.2×10^{-5} and 8.1×10^{-5} cm^2/s, respectively. The solid−liquid mass transfer coefficients for both A and B were calculated from the limiting value of the Sherwood number (e.g., $Sh_D = k_{SL-D}d_p/D_{DB}$) of 2. The actual Sherwood numbers are typically higher by order of magnitude in well-agitated systems but for conservative estimations a value of 2 is taken. The solid−liquid mass-transfer coefficients k_{SL-A} and k_{SL-B} values were obtained as 1.73×10^{-3} and 2.70×10^{-3} cm/s, respectively. The initial rate of reaction was calculated from the conversion profiles. A typical calculation shows that for a typical initial rate of reaction was calculated as 1.64×10^{-7} mol·cm^{-3}·s^{-1}. Therefore, putting the appropriate values in eq 8, the respective values are:

$$6.097 \times 10^6 \gg 7.49 \times 10^4 \quad \text{and} \quad 4.80 \times 10^3$$

The above inequality demonstrates that there is an absence of resistance due to the solid−liquid external mass transfer for both the species D and B and the rate may be either surface-reaction-controlled or intraparticle-diffusion-controlled. Therefore, the effects of catalyst loading at a fixed particle size and temperature were studied to ascertain the influence of intraparticle resistance.

The average particle diameter of the catalyst used in the reactions was 0.06 cm, and thus a theoretical calculation was done on the basis of the Wiesz−Prater criterion to assess the influence of intraparticle diffusion resistance.[41]

According to the Wiesz−Prater criterion, the dimensionless parameter C_{wp} which represents the ratio of the intrinsic reaction rate to intraparticle diffusion rate, can be evaluated from the observed rate of reaction, the particle radius (R_p), effective diffusivity of the limiting reactant (D_e) and concentration of the reactant at the external surface of the particle.

$$\text{(i) If } C_{wp} = r_{obs}\rho_p R_P^{\,2}/D_e[D_s] \gg 1 \tag{10a}$$

then the reaction is limited by severe internal diffusion resistance,

$$\text{(ii) If } C_{wp} \ll 1 \tag{10b}$$

then the reaction is intrinsically kinetically controlled

The effective diffusivity of 1-dodecene (D_{e-D}) inside the pores of the catalyst was obtained from the bulk diffusivity (D_{DB}), porosity (ϵ) and tortuosity (τ) as 6.5×10^{-6} cm^2/s where $D_{e-A} = D_{AB}\epsilon/\tau$. In the present case, the value of C_{wp} was calculated as 0.0235 for the initial observed rate, and therefore the reaction is intrinsically kinetically controlled. However, in a separate experiment, the particles of DTP/K-10 were crushed and sieved and used for the reaction. At the same loading of catalyst, for average particle size of 125 μm, practically the same conversion and selectivity was obtained. This also supported the theoretical calculations. A further proof of the absence of the intraparticle diffusion resistance was obtained through the study of the effect of temperature, and it will be discussed later.

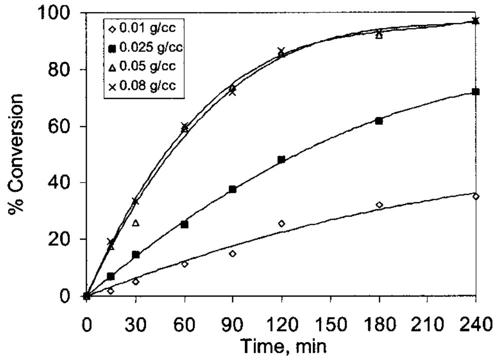


Figure 3. **Effect of catalyst loading on benzene alkylation with 1-dodecene. C_{12}:C_6H_6, 1:10 mol; catalyst DTP/K-10, 0.05 g/mL, temperature, 150 °C; speed, 1000 rpm; reaction time, 4 h.**

Effect of Catalyst Loading. Figure 3 shows the effect of catalyst loading on the alkylation of benzene with 1-dodecene. The catalyst loading was varied over 8-fold from 0.01 to 0.08 g/cm^3. It was found that the yield of dodecylbenzenes increased with increase in the catalyst loading. Rate of alkylation was very slow with 0.01 g/cm^3 catalyst loading, and only 35% conversion of 1-dodecene was obtained. When catalyst loading was increased from 0.05 to 0.08 g/cm^3, the rate of reaction was almost the same, and 97% yields of dodecylbenzene were obtained in both cases. This could be because of the fact that beyond a certain loading, there existed an excess of catalyst sites greater than actually required by the reactant molecules. Hence, there was leveling off of the reaction rate. As shown by eqs 5 and 6, at steady state, the rate of external mass transfer (i.e., from the bulk liquid phase in which D and B are located with concentration [D_0] and [B_0], respectively) to the exterior surface of the catalyst is proportional to a_P, the exterior surface area of the catalyst where the concentrations of D and B are [D_S] and [B_S], respectively. For a spherical particle, a_P is also proportional to w, the catalyst loading per unit liquid volume as shown by eq 9. It is possible to calculate the values of [D_S] and [B_S]. For instance,

$$k_{SL-A}a_p\{[D_o] - [D_S]\} = r_{obs} \text{ at steady state}$$
$$= 1.64 \times 10^{-7}\,\text{mol·cm}^{-3}\text{·s}^{-1}$$

Thus, putting the appropriate values, it is seen that [D_S] $\approx$ [D_0], similarly [B_S] $\approx$ [B_0]. Thus, any further addition of catalyst is not going to be of any consequence for external mass transfer.

Effect of Concentration of Reactants. The concentrations of benzene and 1-dodecene were the important variables. An excess of benzene favoured only the formation of monoalkylated derivatives (Table 2), whereas when the mol ratio of benzene/1-dodecene was decreased from 1:10 to 1:5 as shown in Figure 4, the conversion of 1-dodecene was reduced from 97 to 92%. However, this was marginal, and

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[40] Reid, R. C.; Prausnitz, M. J.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

[41] Fogler, H. S. *Elements of Chemical Reaction Engineering*; Prentice-Hall: New Delhi, 1995.

Table 2. **Effect of mol ratio on alkylation of benzene with 1-dodecene[a]**

C_{12}:C_6H_6 mol	% conversion of C_{12}	% product distribution	
		D.B.	D.D.B.
1:10	97	100	–
1:5	92	100	–
1:2	78	86	14
2:1	67	49	51
5:1	55	40	60

[a] Conditions: catalyst 20% w/w DTP/K-10 0.05 g/cm^3, temperature 150 °C, speed 1000 rpm, reaction time 4 h. Autoclaved.

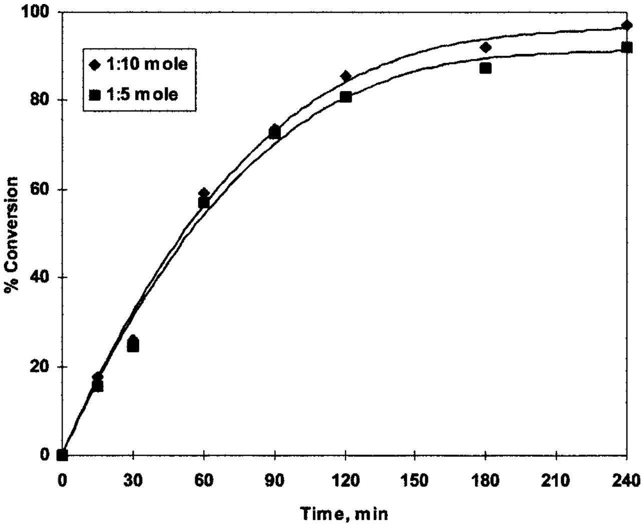


Figure 4. **Effect of mol ratio on benzene alkylation with 1-dodecene. Catalyst DTP/K-10, 0.05 g/mL, temperature, 150 °C; speed, 1000 rpm; reaction time, 4 h.**

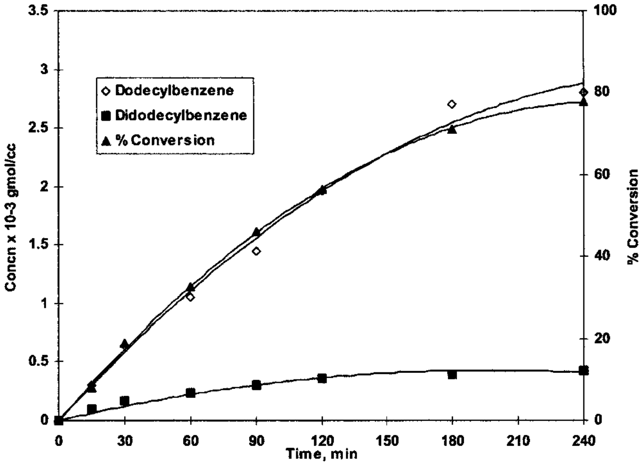


Figure 5. **Effect of mol ratio on yields of mono- and dialkylated products in benzene alkylation with 1-dodecene. C_{12}:C_6H_6, 1:2 mol; catalyst DTP/K-10, 0.05 g/mL, temperature, 150 °C; speed, 1000 rpm; reaction time, 4 h.**

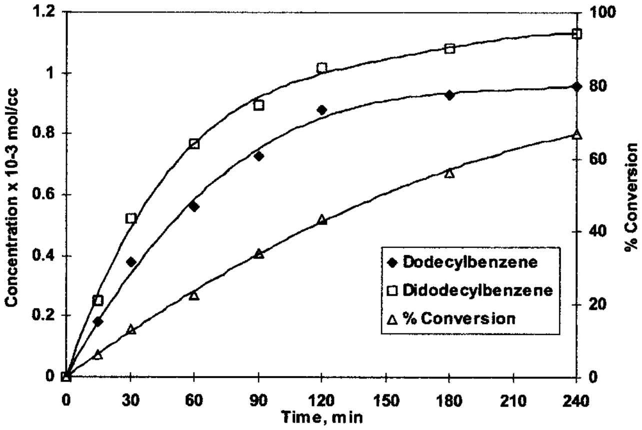


Figure 6. **Effect of mol ratio on yields of mono- and dialkylated products in benzene alkylation with 1-dodecene. C_{12}:C_6H_6, 2:1 mol; catalyst DTP/K-10, 0.05 g/mL, temperature, 150 °C; speed, 1000 rpm; reaction time, 4 h.**

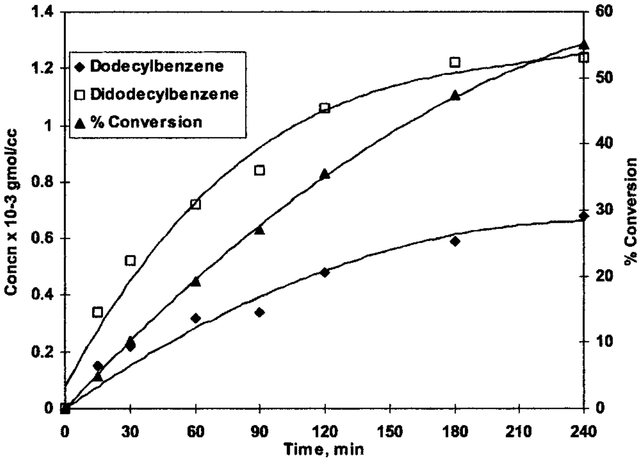
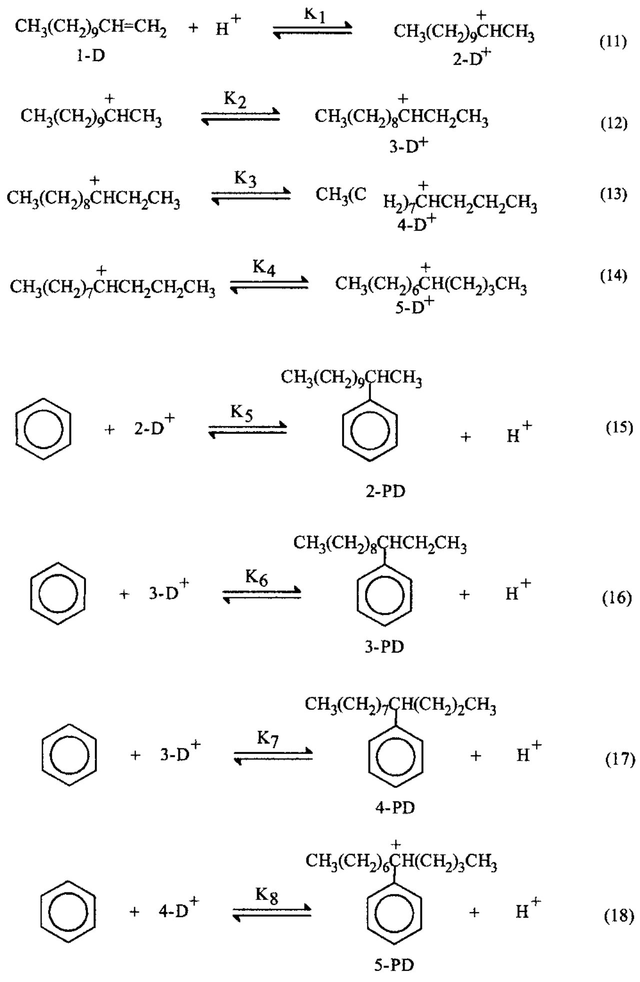


Figure 7. **Effect of mol ratio on yields of mono- and dialkylated products in benzene alkylation with 1-dodecene. C_{12}:C_6H_6, 5:1 mol; catalyst DTP/K-10, 0.05 g/mL, temperature, 150 °C; speed, 1000 rpm; reaction time, 4 h.**

the formation of didodecylbenzene was not still observed. Didodecylbenzene was formed only when the 1-dodecene-to-benzene mol ratio was further reduced to 1:2. The rate of formation of didodecylbenzene was very slow compared to the formation of dodecylbenzene (Figure 5). With a decrease in the mol ratio of 1-dodecene to benzene, the formation of didodecylbenzene had increased, particularly below a mol ratio of 1:5. Figure 6 shows the conversions of the limiting reactant when 1-dodecene-to-benzene mol ratio was increased to 2:1. Conversion to the alkylated product was 67% and selectivities of monoalkylated and dialkylated products were 49 and 51%, respectively. When the 1-dodecene-to-benzene mol ratio was changed to 5:1 (Figure 7) the selectivity of didodecylbenzene had increased to 60% with 55% conversion of 1-dodecene. Thus, in the presence of excess of 1-dodecene, the rate formation of didodecylbenzene was higher than the formation of dodecylbenzene.

Reaction Mechanism and Modeling. In the absence of any external or internal mass transfer limitations, the reaction would be controlled by chemisorption, surface reaction or desorption of products all on the internal pore surface of the catalyst. The initial experiments showed that amongst all possible isomers, only 2-, 3-, 4-, and 5-phenyldodecanes were formed. The formation of these isomers was likely either (i) by the isomerisation of 1-dodecene to 2-, 3-, 4-, and 5-dodecenes when the carbenium ion is formed upon chemisorption of 1-dodecene on the catalyst surface or (ii) by the isomerisation of 1-phenyldodecane which is formed first. However, the concentration profiles of the various phenyldodecanes showed that the possibility (ii) did not arise.

Scheme 2. **Mechanism of formation of linear phenyldodecanes**



By denoting acidic sites on the catalyst surface as H^+ irrespective of their distinction between Brønsted and Lewis sites, the following reactions are thus depicted in Scheme 2.

The formation of didodecylbenzene can take place as per the following:

$$m\text{-PD} + n\text{-D}^+ \overset{K_{15}}{\rightleftharpoons} \text{DDB} + \text{H}^+ \qquad (19)$$

where m = 2, 3, 4, 5 and n = 2, 3, 4, 5, Ks are equilibrium constants.

As shown in Figure 1, when benzene was taken in excess with 20% DTP/K-10 as the catalyst, only the phenyldodecanes are formed without any didodecylbenzene or oligomers 1-dodecene. However, when the mol ratio of 1-dodecene to benzene was 1:2, there was substantial formation of didodecylbenzene (Table 2).

It is thus clear that the carbenium ion formation as shown by eqs 11−14 are equilibrium reactions. Analysis of products had shown that in the cases of reactions 15−18, only the forward rates were significant initially and reaction 19 did occur.

The net rate of forward reactions of benzene is:

$$\begin{aligned} -r_B = \frac{-dC_B}{dt} &= (k_5C_{2-D^+} + k_6C_{3-D^+} + k_7C_{4-D^+} + k_8C_{5-D^+})C_B \\ &= (k_5k_1C_{1-D}C_{H^+} + k_6k_3k_1C_{1-D}C_{H^+} + k_7k_3k_2k_1C_{1-D}D_{H^+} + \\ &\qquad k_8k_4k_3k_2k_1C_{1-D}C_{H^+})C_B \\ &= (k'_5 + k'_6 + k'_7 + k'_8)C_{1-D}C_BC_{H^+} \end{aligned} \qquad (20)$$

where, with the corresponding k as forward rate constants, the following constants are defined.

$$k'_5 = k_5K_1 \qquad (21)$$

$$k'_6 = k_6K_2K_1 \qquad (22)$$

$$k'_7 = k_7K_3K_2K_1 \qquad (23)$$

$$k'_8 = k_8K_4K_3K_2K_1 \qquad (24)$$

$$k_p = k'_5 + k'_6 + k'_7 + k'_8, \quad \text{overall pseudo-constant.} \qquad (25)$$

The net rate of formation of m-PD is given by:

$$\frac{dC_{m-PD}}{dt} = k_pC_{1-D}C_BC_{H^+} - k_{15}C_{m-PD}C_{n-D^+} \qquad (26)$$

The formation of DBB is given by:

$$\frac{dC_{DDB}}{dt} = k_{15}C_{m-PD}C_{n-D^+} \qquad (27)$$

The rates of formations of individuals phenyldodecanes can also found

$$r_{2-PD} = \frac{dC_{2-PD}}{dt} = k'_5C_{1-D}C_BC_{H^+} \qquad (28)$$

$$r_{3-PD} = \frac{dC_{3-PD}}{dt} = k'_6C_{1-D}C_BC_{H^+} \qquad (29)$$

$$r_{4-PD} = \frac{dC_{4-PD}}{dt} = k'_7C_{1-D}C_BC_{H^+} \qquad (30)$$

$$r_{5-PD} = \frac{dC_{5-PD}}{dt} = k'_8C_{1-D}C_BC_{H^+} \qquad (31)$$

The concentration of the acid centres will be in terms of g-catalyst per cm^3 organic phase. Thus, k'_5, k'_6, k'_7, k'_8, and k_p will have units of $cm^6 \cdot mol^{-1} \cdot s^{-1} \cdot gcat^{-1}$.

Validation of Model with Experimental Data and Establishment of Kinetics. When the mol ratio of benzene to 1-dodecene was greater than 5, it could be safely assumed to be a pseudo-first-order reaction for a fixed catalyst concentration. Thus, eq 20 can be written as,

$$\begin{aligned} \frac{-dC_B}{dt} &= k_pC_{1-D}C_{B_0}w \\ &= \frac{-dC_{1-D}}{dt} = (k_pC_{B_0}w)C_{1-D} \end{aligned} \qquad (32)$$

which in terms of fractional conversion and integration leads to

$$-\ln(1 - X) = k_pC_{B0}wt = k_0wt = k_1t \qquad (33)$$

where X = fractional conversion of 1-dodecane. A plot of the left-hand side terms of eq 33 against t will be a straight

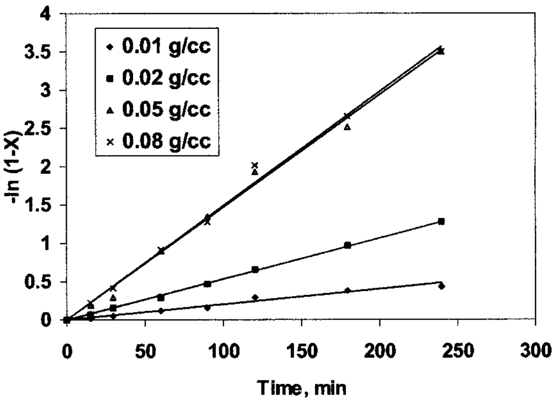


Figure 8. **Plot of −ln(1 − X) vs time at different catalyst loading.**

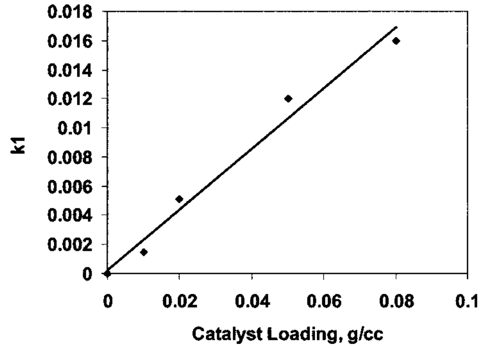


Figure 9. **Plot of k_1 vs catalyst loading.**

line passing through origin with a slope of $k_1 = k_0 w = k_p C_{B_0} w$, from which k_p could be established. Furthermore, k'_5, k'_6, k'_7, and k'_8 can be found from initial rate data.

A plot of $-\ln(1 - X)$ versus t is made for different catalyst loadings in Figure 8 which are all straight lines passing through origin, the slopes of which are plotted against catalyst loading (w) in Figure 9, which shows that the rates are linearly proportional to catalyst loading.

From Figure 1, the initial rates of formation of 2-, 3-, 4-, and 5- phenyldodecanes were obtained and used to calculate the corresponding individual rate constants. The rate constants k'_5, k'_6, k'_7, and k'_8 for the formation of different isomers were found to be, 0.00372, 0.0109, 0.00014, and 0.00006 cm•^{6}gmol^{-1}•gcat^{-1}•s^{-1}, respectively at 150 °C. Again from the slope of Figure 9 the overall reaction rate constant k_p at 150 °C is found to be 0.015 cm•^{6}gmol^{-1}•gcat^{-1}•s^{-1}, which is very close to the sum of the individual reaction rate constants confirming the validity of the model.

Effect of Temperature. At low temperature (120 °C), the conversion of 1-dodecene was 43%. It was found that no dialkylated product was found even when the temperature was increased from 120 to 150 °C (Figure 10). This was because of the presence of excess benzene in the reaction mixture. Plots of $-\ln(1 - X)$ versus t at different temperatures are shown in Figure 11 for 1:10 mol/mol of 1-dodecene to benzene. The slopes of the straight lines represent rate constant k_p at different temperatures. The Arrhenius plot for $\ln(k_p)$ versus $1/T$ (K^{-1}) is shown in Figure 12 from which the apparent activation energy of the reaction is found to be 20.06 kcal/mol.

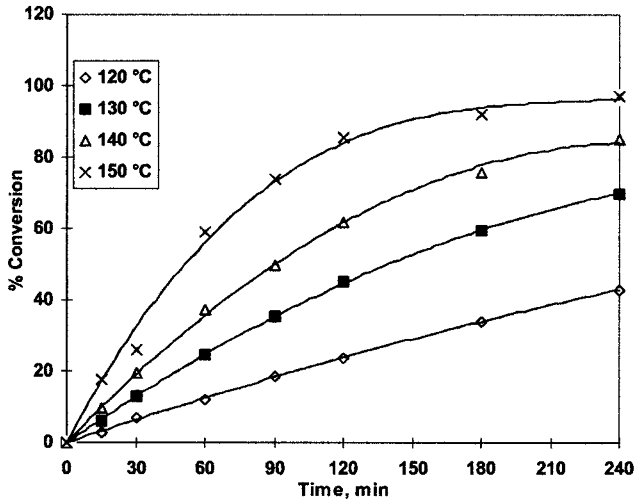


Figure 10. **Effect of temperature on benzene alkylation with with 1-dodecene. C_{12}:C_6H_6, 1:10 mol; catalyst DTP/K-10, 0.05 g/mL, temperature, 150 °C; speed, 1000 rpm; reaction time, 4 h.**

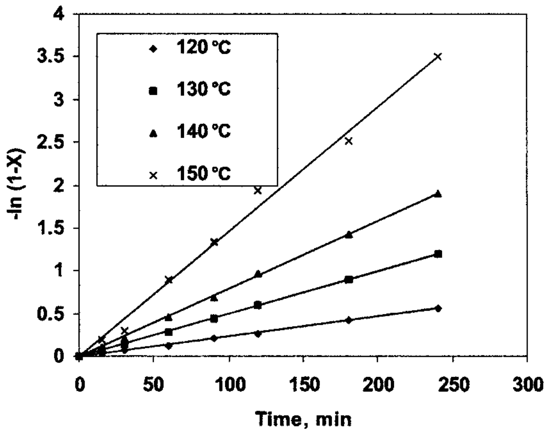


Figure 11. **Plot of −ln(1 − X) vs time at different temperatures.**

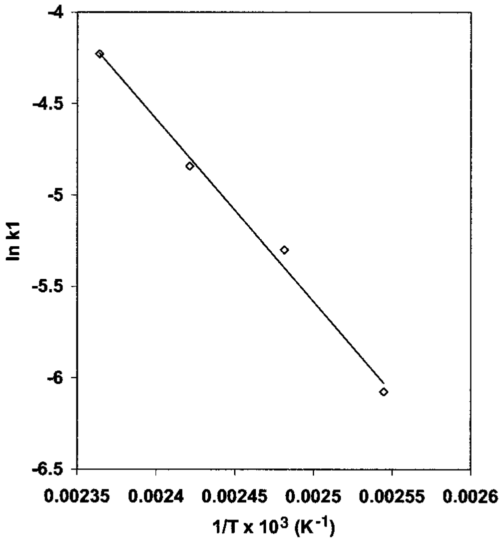


Figure 12. **Arrhenius plot.**

Reusability of Catalyst. Reusability of 20% DTP/K-10 and K-10 was examined for three experiments. After each run, both the catalysts were thoroughly washed with hexane and dried at 120 °C for 2 h prior to reuse. In the presence of

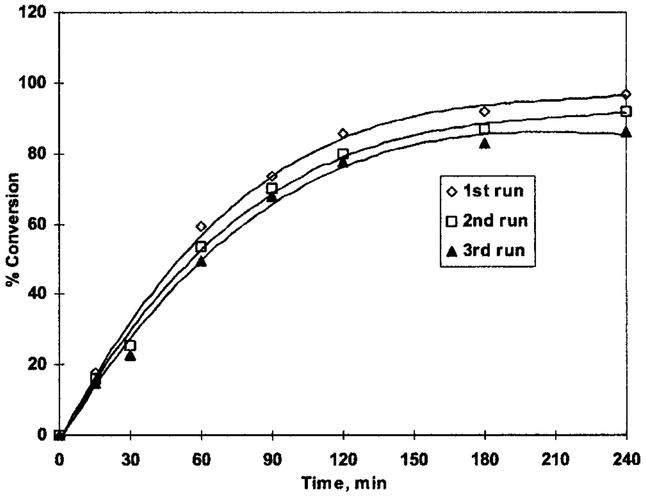


Figure 13. **Reusability of DTP/K-10 on benzene alkylation with with 1-dodecene. Olefin:benzene, 1:10 mol; temperature, 150 °C; catalyst load, 0.05 g/mL; rpm, 1000; reaction time 2 h.**

Table 3. **Reusability of 20% DTP/K-10 on alkylation of benzene with 1-dodecene**[a]

run	% conversion of C_{12}	% 2 - P.D.	% 3 - P.D.
1	97	62	34
2	92	62	32
3	86	60	32

[a] Conditions: catalyst loading 0.05 g/cm^3, temperature 150 °C, speed 1000 rpm, reaction time 4 h. Autoclaved.

DTP/K-10, the conversion of 1-dodecene was reduced to an extent of 11% from the first run to the third run (Figure 13), whereas K-10 clay deactivated to an extent of 23% after three runs without much change in the selectivity of 2-phenyldodecane as shown in Table 3.

Alkylation of Benzene with Other Olefins. To investigate the effect of chain length of α-olefins, the benzene alkylation was also carried out with 1-octene, 1-decene, and 1-tetradecene under otherwise similar conditions. It was found that the rate of benzene alkylation decreased with an increase in the chain length of α-olefin (Figure 14). With 1-octene and 1-decene the rate of reaction was very fast compared to that of 1-tetradecene; 98% conversions of both 1-octene and 1-decene were obtained in 50 and 120 min, respectively. With 1-tetradecene, being a bulky molecule, the rate of reaction was very slow, and conversion to monoalkylated product (tetradecylbenzene) was only 49%.

Conclusions

The alkylation of benzene with 1-dodecene was examined by using 13 different catalysts such as K-10 clay, 20% w/w

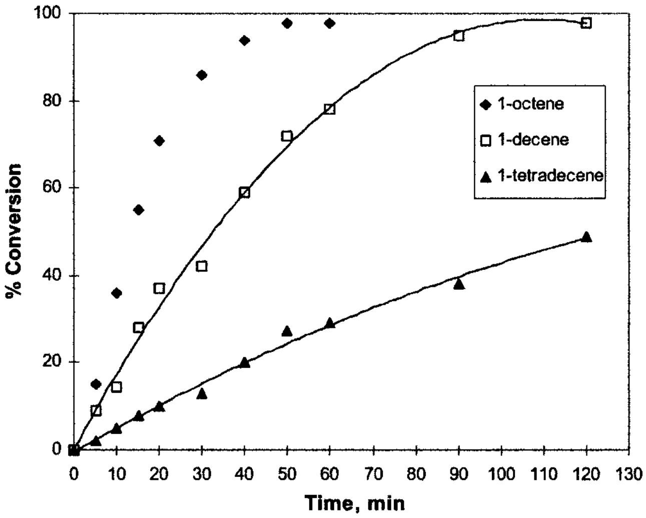


Figure 14. **Alkylation of benzene with different olefins. Olefin: benzene, 1:10 mol; temperature, 150 °C; catalyst load, 0.05 g/mL; rpm, 1000; reaction time 2 h.**

heteropolyacids such as dodecatungstophosphoric acid (DTP), dodecatungstosilicic acid (DTS), and dodecamolybdophosphoric acid (DMP) supported on K-10 clay, Filtrol-24, Al-pillared clay, 20% DTP/silica,10% $AlCl_3$/10% $FeCl_3$/K-10, DTP, Cr-exchanged K-10, Sulphated-zirconia, Zr-exchanged K-10, and 20% DTP/activated carbon. Of all other catalysts used 20% w/w DTP/K-10 clay led to best activity and selectivity to 2- and 3-phenyldodecanes. A mol ratio for benzene/1-dodecene of 10:1, favoured the formation of linear phenyldodecanes. However, with decreasing benzene concentration, the formation of didodecylbenzene had increased. A mechanistic model was built and validated against experimental data.

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