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Alkylation of hydroquinone with methyl-*tert*-butyl-ether and *tert*-butanol

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Abstract

The alkylation of hydroquinone yields industrially important compounds, amongst which *tert*-butylhydroquinone is a very important precursor for its use in pharmaceuticals and in developing photographic plates. Twenty per cent (w/w) dodecatungstophosphoric acid supported on K10 montmorillonite clay (DTP/K10) was found to be a very efficient and novel catalyst in comparison with several others for alkylation of hydroquinone with different alkylating agents such as methyl-*tert*-butyl-ether (MTBE) and *tert*-butanol at 150°C in an autoclave. A summary of characterisation of DTP/K10 is provided and related to the activity. Various reaction parameters were also investigated and a kinetic model was built. The rate of alkylation with MTBE was much faster than that with *tert*-butanol. The reaction follows a typical second order kinetics at a fixed catalyst loading with weak adsorption of both the species. The energy of activation was found to be 19.34 kcal/mol.

Keywords: Alkylation; Hydroquinone; Methyl-*tert*-butyl-ether; *tert*-Butanol; 2-*tert*-Butylhydroquinone; 2,5-Di-*tert*-butylhydroquinone; Heteropolyacids; Catalysis; Dodecatungstophosphoric acid

1. Introduction

The alkylation of hydroquinone yields industrially important compounds. Acid catalysis can be employed with appropriate reaction conditions to get either *C*- or *O*-alkylated products which are useful in a variety industries. Among *C*-alkylation, *tert*-butylhydroquinones are widely used as antioxidants and stabilisers for oils, fats, plastics and rubbers [1]. 2-*tert*-Butylhydroquinone is a very important precursor for its use in pharmaceuticals and in developing photographic plates. Generally it is prepared by alkylation of hydroquinone with isobutylene. Most of the information is patented.

2-*tert*-Butylhydroquinone can be synthesised in high yield by treating hydroquinone with isobutylene in the presence of 65% aqueous H_3PO_4 at 105°C [2,3]. Phase transfer catalysts are also employed to obtain a high yield of 2-*tert*-butylhydroquinone under mild conditions [4]. On the contrary, silica gel is found to be an attractive catalyst for alkylation of hydroquinone, phenol and anisole [5]. Young and Campbell [6] have reported the alkylation of catechol and other phenols with branched alkenes in the presence of Amberlyst-15 as a catalyst. The olefins used were 2-methyl-1-undecene, 2-butyl-1-butene, etc. and that the products formed in the temperature range 85–145°C were 4-alkyl and 3-alkyl catechol, the former being the major product. Fujita et al. [7]

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claimed a process for alkylation of phenols and naphthols with ion exchanged layered catalysts such as aluminium ion exchanged tetra silicic mica, which was superior to Y-type zeolite. Kroupa et al. [1] have carried out the alkylation of benzenediols with excess of methyl-*tert*-butyl-ether (MTBE) at low temperatures between 25 and 35°C in the presence of H_2SO_4 as catalyst. They found 3,5-di-*tert*-butyl benzenediols (72%) as a major product. 4-*tert*-Butyl catechol was obtained in high yields, by reacting catechol and isobutylene in the presence of activated clay having cation exchange capacity of 0.25 meq/g and $H_0 \leq -5.6$ [8]. Merger and Nestler [9] claimed 96% selectivity towards 2-*tert*-butyl *p*-cresol when *p*-cresol was alkylated with MTBE in the presence of Lewasorb AC-10 resin at 90°C.

The alkylation of hydroquinone was thus considered as an important problem necessitating use of different solid acid catalysts and feedstock. Due to the problems associated with unavailability, transportation and handling of isobutylene, particularly for usage in low-tonnage fine chemical and speciality manufacture, it is advantageous to generate pure isobutylene in situ. Two attractive sources of isobutylene are *tert*-butanol and MTBE. *tert*-Butanol is available as a by-product in the ARCO process for propylene oxide. The cracking of MTBE for the generation of isobutylene has been discussed [10–13]. MTBE is a good source for the generation of pure isobutylene and the by-product, methanol, is also a very important raw material in chemical industry. 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 the alkylating agent [14,15]. Synthesis of MTBE from *tert*-butanol and methanol has been studied in this laboratory by using a variety of solid acids [15]. Heteropoly acids (HPAs) supported on clays have shown superior activity as catalyst in comparison to others in the alkylation and etherification reactions [15–17].

It is thus clear that there is tremendous scope for devising a new catalytic process for the synthesis of *tert*-butylhydroquinone. In the present study, alkylation of hydroquinone was carried out with MTBE and *tert*-butanol in the presence of solid acidic catalysts. Since homogeneous catalysts are the source of pollution, various solid acidic catalysts such as HPA, K10 montmorillonite clay, different HPAs supported on K10, $ZnCl_2$ supported on K10 (clayzic), sulphated zirconia, etc. were evaluated to achieve maximum selectivity towards 2-*tert*-butylhydroquinone. A kinetic model is also presented.

2. Experimental

2.1. Chemicals and catalysts

MTBE was obtained from Texas Petrochemicals, USA. K10 clay was obtained from Fluka, Germany. Filtrol-24 was obtained from Engelhard. Hydroquinone and other chemicals were obtained from M/s s.d. Fine Chemicals, Mumbai, India and used without further purification.

2.2. Sulphated zirconia

Sulphated zirconia was prepared by a well established procedure in this laboratory [18,19].

2.3. Preparation of dodecatungstophosphoric acid supported on K10

K10 montmorillonite was dried in an oven at 120°C for 2 h prior to its use as support. After drying, 4 g of K10 was weighed accurately. To prepare a catalyst with 20% loading of dodecatungstophosphoric acid (DTP), 1 g of DTP was dissolved in 4 ml of dry methanol. This volume of solvent used was approximately equal to the pore volume of the catalyst. This solution was added dropwise to predried K10 (4 g) with constant stirring with glass rod. Initially on addition up to DTP solution, the clay was in the powdery form, but on further addition of DTP solution it formed the paste. The paste on further stirring for 10 min resulted in a free flowing powder. It was then dried in an oven at 120°C for 2 h and subsequently calcined at 285°C for 3 h. Similarly other heteropoly acids such as dodecatungstosilicic acid and dodecaphosphomolybdic acid were also impregnated on K10 montmorillonite. Supported catalyst with different loading of DTP (5, 10 and 40%) was also prepared by this method. 20% $ZnCl_2$ supported on Filtrol-24 clay was also prepared by incipient wetness technique.

3. Reaction studies

3.1. Apparatus and procedure

All experiments were carried out in a 100 ml stainless steel autoclave manufactured by Parr Instruments, USA. A four-bladed-pitched turbine impeller was used for agitation. The temperature was maintained at $\pm 1^\circ$C of the desired value. Predetermined quantities of reactants and the catalyst were charged into the autoclave and the temperature was raised to the desired value. Once the temperature was attained, the initial sample was withdrawn which was the zero time sample. Further samples were drawn at periodic intervals.

A typical standard experiment consisted of 0.1 mol of hydroquinone, 0.3 mol of MTBE and 20% (w/w) catalyst, based on the weight of hydroquinone and 1,4-dioxan was used as solvent to make up the volume 50 ml. The temperature was maintained at 150°C and the speed of agitation was 1000 rpm.

3.2. Analysis

Analysis of the reaction mixture was done on a high pressure liquid chromatogram (Tosho) with the conditions mentioned below:

- Column: Novopak-C-18.
- Mobile phase: methanol:water (60:40).
- Detector wavelength: 293 nm.
- Flow rate of mobile phase: 1 ml/min.

The samples were analysed for hydroquinone, 2-*tert*-butylhydroquinone and 2,5-di-*tert*-butylhydroquinone. Identification of products was done by matching the retention time of reaction products to the authentic compounds. 2-*tert*-Butylhydroquinone and 2,5-di-*tert*-butylhydroquinone were also separated by using preparative thin layer chromatography. Silica gel 60 F_{254}, precoated on aluminium sheet was used as stationary phase and solvent system such as benzene:ether (90:10) was used to separate the compounds.

4. Reaction scheme

In the presence of an acid catalyst, MTBE cracks into isobutylene and methanol. Isobutylene thus produced reacts in situ with hydroquinone to give 2-*tert*-butylhydroquinone (2-TBHQ) and 2,5-di-*tert*-butylhydroquinone (2,5-DTBHQ). Further dimer and trimer of isobutylene can also be formed as side products. Although under the reaction conditions, there was negligible formation of these products. The reaction network is shown in Scheme 1.

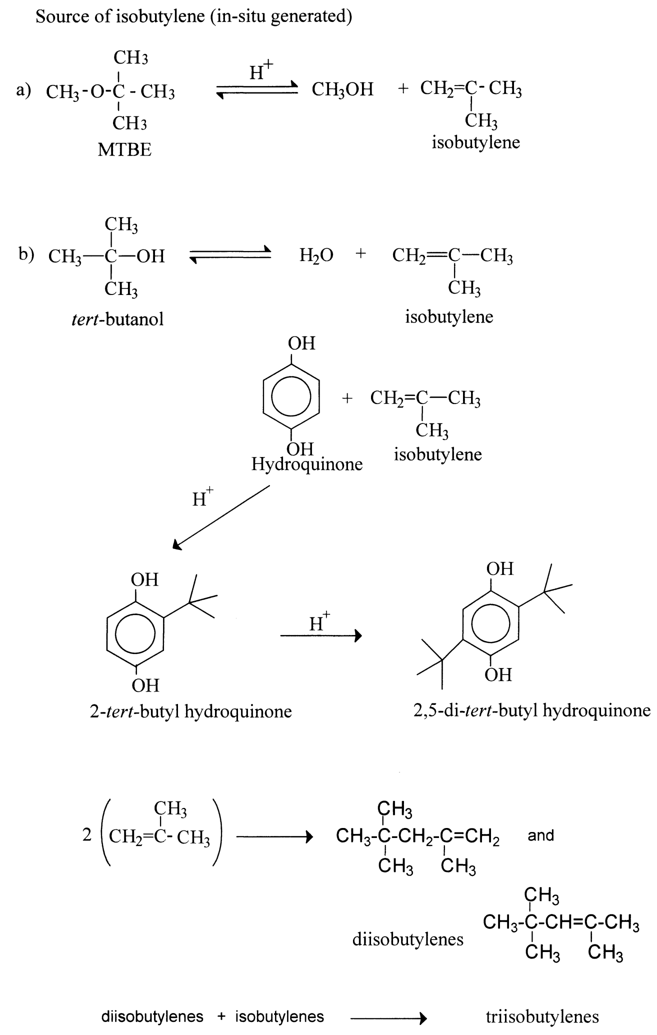
5. Results and discussions

5.1. Efficacies of various catalysts

In this work the performance of six solid acid catalysts was evaluated for the alkylation of hydroquinone with MTBE, in the absence of mass transfer resistance (Table 1). A good cracking catalyst and a poor alkylation catalyst would result in loss of the generated isobutylene. A reverse phenomenon would result in poor yield of the required alkylated product. It was therefore necessary that the best catalyst should give a reasonable activity for the cracking of MTBE or dehydration of *tert*-butanol as well as the alkylation of hydroquinone with isobutylene generated in situ. Further, it is also essential that the rate of alkylation is faster than that of oligomerisation of the isobutylene generated in situ to get maximum selectivity of the alkylated product.

Heteropoly acids such as DTP and dodecatungstosilicic acid (DTS) supported on K10 montmorillonite gave good conversion of hydroquinone (46 and 42%, respectively). However, the maximum selectivity towards 2-*tert*-butylhydroquinone (72%) was obtained in the case of 20% DTP/K10 as catalyst. Clayzic (20% $ZnCl_2$/K-10) and 20% DTP supported on clayzic gave 26 and 24% conversion of hydroquinone. K10 clay, clayzic and sulphated zirconia (S–ZrO_2) gave lower conversions but 100% yield of 2-*tert*-butylhydroquinone.

The use of MTBE as a butylating agent is advantageous. MTBE cracking starts beyond 75°C in a significant way and no *O*-alkylated product is formed. Whatever isobutylene is generated in situ is consumed leading to *C*-alkylated product and no free isobutylene in the gas phase is noticed nor any oligomerisation takes place at low temperatures. The co-product methanol is recyclable. In earlier studies, we had noticed that no *O*-alkylated product is formed beyond 50°C when *p*-cresol was alkylated with isobutylene in the pres-



Scheme 1. Reaction scheme for alkylation of hydroquinone with MTBE.

ence of sulphated zirconia and UDCaT-1 as catalysts [14,19], since the rate of *C*-alkylation was very much faster than that of oligomerisation. In the present case, all standard experiments were done at 150°C and the analysis showed no *O*-alkylated product was formed. No ethers of hydroquinone with methanol were formed and there was no self-condensation of hydroquinone as indicated by spectroscopic analysis and isolation of products. In the case of MTBE as alkylating agent the conversion of hydroquinone with 1:3 mole ratio was limited to less than 50% in order that the isobutylene formation was not excessive to produce the oligomers.

The effect of alkylating agent on the rate of alkylation was done with 20% DTP/K10 as catalyst by employing *tert*-butanol as alkylating agent under otherwise similar conditions. The conversion of hydroquinone was found to be 23% with 100% selectivity of 2-TBHQ. The conversion is much lower by a factor of 2 than that in case of MTBE. *tert*-Butanol cracks into isobutylene and water in the presence of the catalyst. Water thus produced in situ, may have a detrimental effect on catalyst activity resulting in low conversion of hydroquinone. In another study, we had found that there is a decrease in the activity of DTP/K10 whenever water

Table 1
Efficacies of various catalysts in alkylation of hydroquinone with MTBE (hydroquinone:MTBE 1:3 mole, catalyst loading 0.014 g/cm^3, temperature 150°C, speed 1000 rpm, solvent 1,4-dioxan, reaction time 4 h, autogeneous pressure 150 psi; DTP: dodecatungstophosphoric acid; DTS: tungstosilicic acid; TBHQ: *tert*-butylhydroquinone; DTBHQ: di-*tert*-butylhydroquinone)

Catalyst	Conversion (%)	Selectivity (%)	
		2-TBHQ	2,5-DTBHQ
DTP (20%)/K10	46	72	28
TSA (20%)/K10	42	42	58
K10 montmorillonite	29	100	–
$ZnCl_2$ (20%)/K10	25	100	–
S–ZrO_2	26	100	–
DTP/$ZnCl_2$/K10	24	89	11

generated in situ exceeded a critical value [13]. Besides, the rate of dehydration of *tert*-butanol could be rate limiting in comparison with that of alkylation and thus only the mono-alkylated product was formed.

5.2. Effect of DTP loading on K10

In order to investigate the change in selectivity of alkylated products, different amounts of DTP were loaded on K10 montmorillonite according to incipient wetness technique. With an increase in DTP loading from 5 to 40% (w/w) of K10, the conversion of hydroquinone also increased (Fig. 1). At high DTP loading (40%), selectivity of 2-*tert*-butylhydroquinone and 2,5-di-*tert*-butylhydroquinone were found to be 45 and 55%, respectively. There was some formation of oligomers of isobutylene. However, further experiments were done with 20% DTP/K10 were the selectivity to the mono-alkylated product was very high and there was no oligomers formed (Table 2).

Since 20% DTP/K10 was the best catalyst, the effects of various parameters on conversion and yields were studied with it. It has already been fully characterised by us [16,17] and a brief summary is provided here. The surface areas of the catalysts measured by nitrogen BET method for K10 montmorillonite and DTP/K10 were found to be 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/K10 may be 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 where the access to smaller pores is denied, thereby leading to the decrease in accessible surface area. The average particle size of both K10 and DTP/K10, as determined by image analysis, was in the range of 600 μm. The XRD studies of DTP/K10 had indicated that in the impregnation process, the clay has lost some of its crystallinity compared to K10. The cation exchange capacity (CEC) of the catalyst was determined by the method to observe that DTP/K10 possesses higher CEC than K10. This may be due to some additional surface protons, which come by way of heteropoly acid impregnation, which may play a role on account of easy availability for the exchange reaction. We have earlier reported [16] that on the basis of the actual quantity of DTP loaded on the support

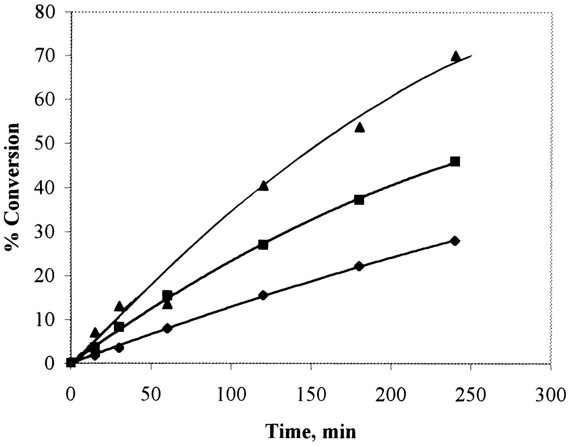


Fig. 1. Effect of catalyst loading on alkylation of hydroquinone with MTBE. Hydroquinone: MTBE 1:3 mole, temperature 150°C, catalyst 20% DTP/K-10, speed 1000 rpm, solvent 1,4 dioxan: (◆) 0.007 g/cm^3; (■) 0.014 g/cm^3; (▲) 0.021 g/cm^3.

Table 2
Effect of DTP loading on K10 in alkylation of hydroquinone with MTBE (hydroquinone:MTBE 1:3 mole, catalyst loading 0.014 g/cm^3, temperature 150°C, speed 1000 rpm, solvent 1,4-dioxan, reaction time 4 h, autogeneous pressure 150 psi)

DTP on K10 (%)	Conversion (%)	Selectivity (%)	
		2-TBHQ	2,5-DTBHQ
DTP (5%)/K10	33	40	60
DTP (10%)/K10	37	66	34
DTP (20%)/K10	46	72	28
DTP (40%)/K10	66	45	55

in comparison with the same unloaded catalyst or the support K10 alone, the turnover frequency is greater in the case of the supported catalyst. Thus, there is a synergism between DTP and K10 leading to higher activity. In the case of DTP/K10 there are lot of dispersed particles on the surface of the support K10 as revealed by SEM photomicrographs. FTIR studies of K10 showed that there was Si–O and Si–O–Al linkages and the OH groups are bonded to the Al atoms, whereas in DTP/K10 indicated the presence of H_3O^+ (Bronsted acidity) and the linkage of phosphorous.

5.3. Effect of speed of agitation

The influence of external mass transfer on the reaction rate was studied by keeping the speed of agitation at 600, 800 and 1000 rpm. It was observed that the conversion of hydroquinone was practically same in all the cases without any change in selectivity. It was demonstrated that this reaction was not influenced by external mass transfer effects. Hence, to be on safer side further reactions were carried out at 1000 rpm. A theoretical analysis of the assessment of external mass transfer resistance is given to support this observation. Details of this theory for general slurry reactions are given elsewhere [19].

This is a typical solid–liquid slurry reaction involving the transfer of hydroquinone the limiting reactant (A) and MTBE (B) from the bulk liquid phase to the catalyst wherein external mass transfer of reactants to the surface of the catalyst particle, followed by intra-particle 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.

$$\mathrm{A}+z\mathrm{B}^{\text{solid}}\overset{\text{catalyst}}{\rightarrow}\text{products} \tag{1}$$

At steady state, the rate of mass transfer per unit volume of the liquid phase (gmol cm^{-3} s^{-1}) is given by

$$R_\mathrm{A}=k_{\mathrm{SL-A}}a_\mathrm{p}\{[\mathrm{A}_0]-[\mathrm{A}_\mathrm{s}]\} \tag{2}$$

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

$$R_\mathrm{B}=k_{\mathrm{SL-B}}a_\mathrm{p}\{[\mathrm{B}_0]-[\mathrm{B}_\mathrm{s}]\} \tag{3}$$

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

$$R_\mathrm{A}=\frac{R_\mathrm{B}}{z}=r_{\mathrm{obs}}(\text{observed rate of reaction within the catalyst particle}) \tag{4}$$

Here the subscripts "0" and "s" denote the concentrations in bulk liquid phase and external surface of catalyst, respectively.

Depending on the relative magnitudes of external resistance to mass transfer and reaction rates, different controlling mechanisms have been put forward [18]. When the external mass transfer resistance is small, then the following inequality holds:

$$\frac{1}{r_{\mathrm{obs}}}\gg\frac{1}{k_{\mathrm{SL-A}}a_\mathrm{p}[\mathrm{A}_0]}\quad\text{and}\quad\frac{1}{zk_{\mathrm{SL-B}}a_\mathrm{p}[\mathrm{B}_0]} \tag{5}$$

The observed rate r_{obs} could be given by three types of models wherein the contribution of intra-particle diffusional resistance could be accounted for by incorporating the effectiveness factor η. These models are

1. the power law model if there is a very weak adsorption of reactant species,
2. Langmuir–Hinselwood–Hougen–Watson model,
3. 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 intra-particle resistance so that a true intrinsic kinetic equation could be used. It is seen that the conversion remains practically the same in the range 600–1000 rpm, which indicates the absence of external solid–liquid mass transfer resistance. Theoretical analysis was also done to ensure that the external mass transfer resistance was indeed absent as delineated below.

According to Eq. (5), it is necessary to calculate the rates of external mass transfer of both hydroquinone (A) and MTBE (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

$$a_\mathrm{P}=\frac{6w}{\rho_\mathrm{P}d_\mathrm{P}} \tag{6}$$

where w is the catalyst loading (g/cm^3) of liquid phase, ρ_p the density of particle (g/cm^3) and d_P is the particle diameter (cm).

For the maximum catalyst loading used (0.021 g/cm^3) for a particle size (d_p) of 0.06 cm, in the current

Table 3
Effect of catalyst loading on alkylation of hydroquinone with MTBE and *tert*-butanol (hydroquinone:MTBE (or *tert*-butanol) 1:3 mole, catalyst DTP (20%)/K10, temperature 150°C, speed 1000 rpm, solvent 1,4-dioxan, reaction time 4 h, autogeneous pressure 150 psi)

Catalyst loading (g/cm^3)	MTBE			*tert*-Butanol		
	Conversion (%)	Selectivity (%)		Conversion (%)	Selectivity (%)	
		2-TBHQ	2,5-DTBHQ		2-TBHQ	2,5-DTBHQ
0.007	28	96	4	10	100	–
0.014	46	72	28	23	100	–
0.021	63	68	32	29	90	10

studies, a_p=2.45 cm^2/cm^3 liquid phase. The liquid phase diffusivity values of the reactants A and B, denoted by D_{AB} and D_{BA}, were calculated by using the Wilke–Chang equation [20] at 150°C as 9.05×10^{-5} and 1.425×10^{-4} 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. $Sh_A=k_{SL-A}d_p/D_{AB}$) 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 [18,19]. The values of the solid–liquid mass transfer coefficients k_{SL-A} and k_{SL-B} were obtained as 3×10^{-3} and 4.75×10^{-3} cm/s, respectively. The initial rate of reaction was calculated from the conversion profiles. A typical calculation shows a typical initial rate of reaction as 1.67×10^{-7} gmol cm^{-3} s^{-1}. Therefore, putting the appropriate values in Eq. (5),

$$\frac{1}{r_{obs}} \gg \frac{1}{k_{SL-A}a_P\,[A_0]} \quad \text{and} \quad \frac{1}{zk_{SL-B}a_P\,[B_0]} \tag{7}$$

i.e., $6.03\times10^6 \gg 5.44\times10^4$ and 1.43×10^4.

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

5.4. Effect of catalyst loading

In the absence of external mass transfer resistance, the rate of reaction is directly proportional to catalyst loading based on the entire liquid phase volume. Alkylation of hydroquinone with MTBE was investigated by varying catalyst loading from 0.007 to 0.021 g/cm^3 (Table 3). It was found that with an increase in catalyst loading, the formation of alkylated product also increased (Fig. 2). At lowest catalyst loading, the conversion of hydroquinone was only 28% which increased to 63% when the loading was 0.021 g/cm^3. The corresponding values obtained, in the presence of *tert*-butanol as alkylating agent, are given in Table 3. Since the conversions with *tert*-butanol are low with *tert*-butanol, only the mono-alkylated product is formed. It appears that the rate of dehydration of *tert*-butanol is slower than the rate of cracking of MTBE.

As shown by Eqs. (1) and (2), at steady state, the rate of external mass transfer (i.e., from the bulk liquid

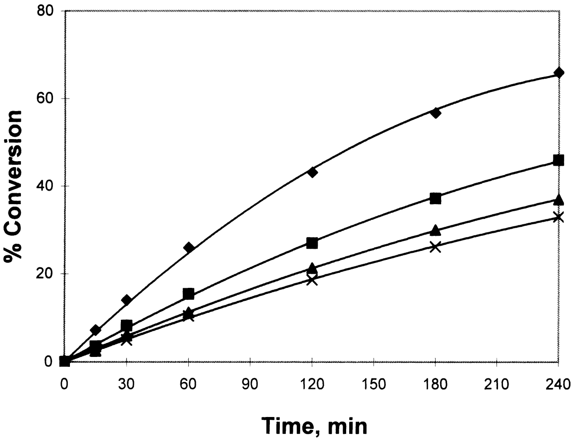


Fig. 2. Effect of DTP loading on alkylation of hydroquinone with MTBE. Hydroquinone: MTBE 1:3 mole, temperature 150°C, catalyst loading 0.014 gm/cm^3, speed 1000 rpm, solvent 1,4 dioxan: (◆) DTP(40%)/K10; (■) DTP(20%)/K10; (▲) DTP(10%)/K10; (×)DTP(5%)/K10.

phase in which A and B are located with concentrations $[A_0]$ 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 A and B are $[A_s]$ 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. (6). It is possible to calculate the values of $[A_s]$ and $[B_s]$. For instance,

$$k_{SL-A}a_p\{[A_0]-[A_s]\}=r_{obs} \text{ at steady state } = 1.67\times10^{-7}\,\text{gmol}\,\text{cm}^{-3}\,\text{s}^{-1} \tag{8}$$

Thus putting the appropriate values, it is seen that $[A_s]\approx[A_0]$, similarly $[B_s]\approx[B_0]$. Thus, any further addition of catalyst is not going to be of any consequence for external mass transfer.

5.4.1. Proof of absence of intra-particle resistance

The average particle diameter of the catalyst used in the reactions was 0.06 cm and thus a theoretical calculation was done based on the Wiesz–Prater criterion to assess the influence of intra-particle diffusional resistance [21].

According to the Wiesz–Prater criterion, the dimensionless parameter C_{wp} which represents the ratio of the intrinsic reaction rate to intra-particle 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:

1. if $C_{wp}=(-r_{obs}\rho_p R_p{}^2)/D_e[A_s]\gg1$ then the reaction is limited by severe internal diffusional resistance,
2. if $C_{wp}\ll1$ then the reaction is intrinsically kinetically controlled.

The effective diffusivity of hydroquinone ($D_{e\text{-}A}$) inside the pores of the catalyst was obtained from the bulk diffusivity (D_{AB}), porosity (ε) and tortuosity (τ) as 1.08×10^{-6} cm²/s, where $D_{e\text{-}A}=(D_{AB}\varepsilon)/\tau$. In the present case, the value of C_{wp} was calculated as 0.039 for the initial observed rate and therefore the reaction is intrinsically kinetically controlled. However, in a separate experiment, the particles of DTP/K10 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 intra-particle diffusion resistance was obtained through the study of the effect of temperature and it will be discussed later.

5.5. Effect of mole ratio

The mole ratio of hydroquinone and MTBE was changed from 1:1 to 1:6 mole under otherwise similar sets of conditions. The conversion of hydroquinone was only 37% when hydroquinone to MTBE mole ratio was 1:1 (Fig. 3). With an increase in mole ratio (1:6), the conversion of hydroquinone increased to 52% and selectivity towards 2,5-di-*tert*-butylhydroquinone also increased to 34% (Table 4). With *tert*-butanol as the alkylating agent, hydroquinone to *tert*-butanol mole ratio was changed from 1:1 to 1:6 under otherwise similar sets of conditions. The conversion of hydroquinone was only 13% when the mole ratio was 1:1. Selectivity of 2-*tert*-butylhydroquinone was 100% even when the mole ratio was increased to 1:3 from 1:1. However, formation of 2,5-di-*tert*-butylhydroquinone was observed when hydroquinone to *tert*-butanol mole ratio was further increased to 1:6 mole because more availability of the alkylating agent to commence the dialkylation product.

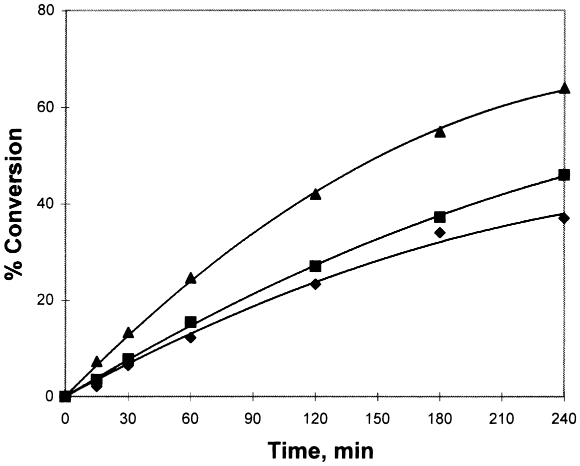


Fig. 3. Effect of mole ratio on alkylation of hydroquinone with MTBE. Catalyst loading 0.014 g/cm³, temperature 150°C, catalyst 20% DTP/K-10, speed 1000 rpm, solvent 1,4 dioxan: (◆) 1:1 mole; (■) 1:3 mole; (▲) 1:6 mole.

Table 4
Effect of mole ratio on alkylation of hydroquinone with MTBE and *tert*-butanol (catalyst DTP (20%)/K10, catalyst loading 0.014 g/cm^3, temperature 150°C, speed 1000 rpm, solvent 1,4-dioxan, reaction time 4 h, autogeneous pressure 150 psi)

Hydroquinone	MTBE			*tert*-Butanol		
	Conversion (%)	Selectivity (%)		Conversion (%)	Selectivity (%)	
		2-TBHQ	2,5-DTBHQ		2-TBHQ	2,5-DTBHQ
1:1 mole	37	96	4	13	100	–
1:3 mole	46	72	28	23	100	–
1:6 mole	52	66	34	31	95	5

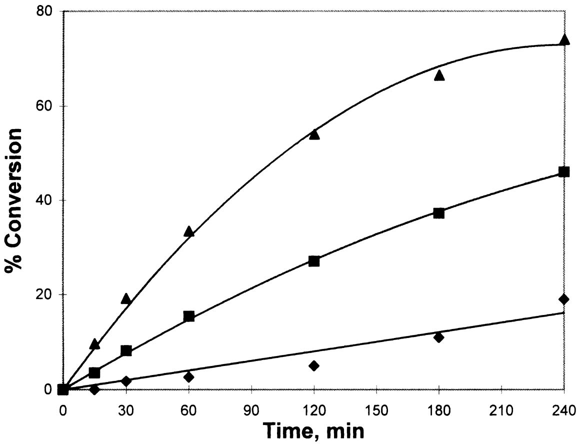


Fig. 4. Effect of temperature on alkylation of hydroquinone with MTBE. Hydroquinone: MTBE 1:3 mole, speed 1000 rpm, catalyst 20% DTP/K-10, catalyst loading 0.014 g/cm^3, solvent 1,4 dioxan: (◆) 130°C; (■) 150°C; (▲) 170°C.

5.6. Effect of temperature

The effect of temperature on the rate of alkylation of hydroquinone was studied in the range 130–170°C (Fig. 4). Increasing temperature resulted in an increase in the conversion of hydroquinone. It was found that at 130°C, the conversion of hydroquinone was only 19% and selectivities of 2-*tert*-butylhydroquinone and 2,5-di-*tert*-butylhydroquinone were 92 and 8%, respectively. Whereas at 170°C, the conversion of hydroquinone increased to 74% and the selectivities of 2-*tert*-butylhydroquinone and 2,5-di-*tert*-butylhydroquinone were 62 and 38%, respectively (Table 5).

In the case of *tert*-butanol as the alkylating agent, it was found that the conversion of hydroquinone was strongly dependent on the reaction temperature. At 130°C, the conversion of hydroquinone was only 10% and there was no formation of 2,5-di-*tert*-butylhydroquinone. At 150°C, the conversion of hydroquinone was 23% which increased to 35% at 170°C at which the selectivity to the mono-alkylated product had suffered marginally (Table 5).

5.7. Effect of reusability of 20% DTP/K10

The reusability of 20% DTP/K10 was tested by employing it three times. After each run the catalyst was washed thoroughly with hexane and dried in an oven

Table 5
Effect of temperature on alkylation of hydroquinone with MTBE and *tert*-butanol (hydroquinone:MTBE (or *tert*-butanol) 1:3 mole, catalyst DTP (20%)/K10, catalyst loading 0.014 g/cm^3, speed 1000 rpm, solvent 1,4-dioxan, reaction time 4 h, autogeneous pressure 150 psi)

Temperature (°C)	MTBE			*tert*-Butanol		
	Conversion (%)	Selectivity (%)		Conversion (%)	Selectivity (%)	
		2-TBHQ	2,5-DTBHQ		2-TBHQ	2,5-DTBHQ
130	19	92	8	10	100	–
150	46	72	28	23	100	–
170	74	62	38	35	92	8

Table 6
Effect of reusability of 20% DTP/K10 on alkylation of hydroquinone with MTBE and *tert*-butanol (hydroquinone:MTBE (or *tert*-butanol) 1:3 mole, catalyst loading 0.014 g/cm^3, temperature 150°C, speed 1000 rpm, solvent 1,4-dioxan, reaction time 4 h, autogeneous pressure 150 psi)

Run No.	Conversion (%)	Selectivity (%)	
		2-TBHQ	2,5-DTBHQ
1	46	72	28
2	46	74	26
3	41	75	25

at 120°C for 2 h. As shown in Table 6, in the presence of fresh catalyst, the conversion of hydroquinone was 46% and the selectivity of 2-*tert*-butylhydroquinone and 2,5-di-*tert*-butylhydroquinone were 72 and 28%, respectively. During the third run, the conversion of hydroquinone decreased to 43% without any significant change in the selectivities of the alkylated products. The catalyst was filtered and then dried and weighed after each run to find that there was up to 5% loss of catalyst during filtration due to attrition and no makeup catalyst was added. Thus the catalyst activity was not deactivated and was reusable.

When an HPA such as DTP is supported on K10, the high activity of the catalyst is obtained which is due to the presence of the HPA on the support. We had reported earlier if the HPA is physically adsorbed on the surface then catalyst cannot be reused because of loss of active sites during usage of catalyst. It was found that the DTP/K10 showed consistent activity to a minimum of three runs even in the presence of highly polar solvent such as methanol and 1,4 dioxane. This is because DTP was chemically bonded to the support. There was no leaching of DTP from the support. We have confirmed the stability of this catalyst in other systems [13,15,16].

Thus it is concluded that DTP was chemically adsorbed on the catalyst surface and no leaching was observed. There was no leaching of DTP from the support and there is no poisoning of the active sites.

5.8. Mechanism and reaction kinetics

Several mechanisms have been considered for the alkylation of *p*-cresol with MTBE by us [14] and the following was found to be adequate to describe the results. Since no dehydration of hydroquinone was found to take place to give the corresponding ether or for that matter no *O*-alkylated product was formed with methanol generated in situ. So this would suggest that there is adsorption of MTBE on the catalytic site which can react with hydroquinone either from the adjacent site or MTBE first gets cracked to isobutylene which is then readsorbed on the catalytic site to react with hydroquinone. The Eley–Rideal mechanism was considered adequate and the rate of alkylation is given by

$$-r_{\mathrm{A}} = \frac{K_{\mathrm{B}}K_{\mathrm{R}}[\mathrm{A}][\mathrm{B}]w}{\{1 + K_{\mathrm{B}}[\mathrm{B}]\}} \qquad (9)$$

where K_{B}, k_{R}, and w are the adsorption equilibrium constant for MTBE, intrinsic rate constant for the reaction in the absence of any external or internal resistance and w is the catalyst loading.

It was found that the weak adsorption of MTBE on the catalytic sites was valid wherein the surface reaction between adsorbed MTBE with hydroquinone from the liquid phase controlled the overall rate of reaction. It could also mean that both species are weakly adsorbed as per the Langmuir–Hinshelwood–Hougen–Watson model. However, the key step is the adsorption of MTBE which is essential for in situ generation of isobutylene. Since there was no dehydration of hydroquinone to form a symmetric ether as was confirmed from the mass balance and spectroscopic analysis, the Eley–Rideal model seems most adequate. Further, since $K_{\mathrm{B}} \ll 1$, Eq. (9) reduces to that for a typical second order kinetic equation

$$-r_{\mathrm{A}} = \frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_2[\mathrm{A}][\mathrm{B}]w \qquad (10)$$

Upon substitution in terms of mole ratio M_{R} of MTBE to hydroquinone and fractional conversion of hydroquinone X_{H}, Eq. (10) can be integrated to the following:

$$\ln\left\{\frac{[M_{\mathrm{R}} - X_{\mathrm{H}}]}{[M_{\mathrm{R}}(1 - X_{\mathrm{H}})]}\right\} = [\mathrm{A}_0](M_{\mathrm{R}}-1)wk_2t = k_0t \qquad (11)$$

where M_{R} is the mole ratio of initial concentration of MTBE to that of hydroquinone, X_{H} the fractional conversion of hydroquinone, $[\mathrm{A}_0]$ the initial concentration of hydroquinone.

Thus plots of $\ln((M_{\mathrm{R}}-X_{\mathrm{H}})/M_{\mathrm{R}}(1-X_{\mathrm{H}}))$ vs time were made for different temperatures as shown

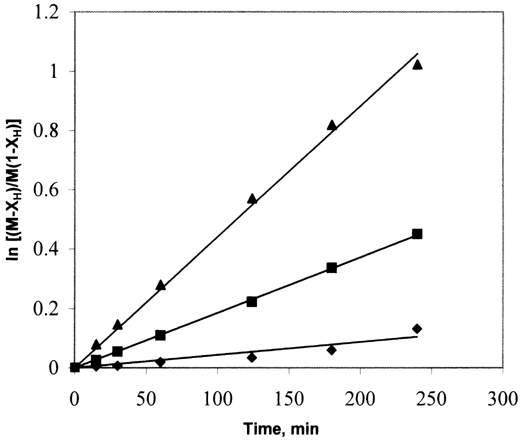


Fig. 5. Plot of $\ln[(M-X_H)/M(1-X_H)]$ vs time: (◆) 130°C; (■) 150°C; (▲) 170°C.

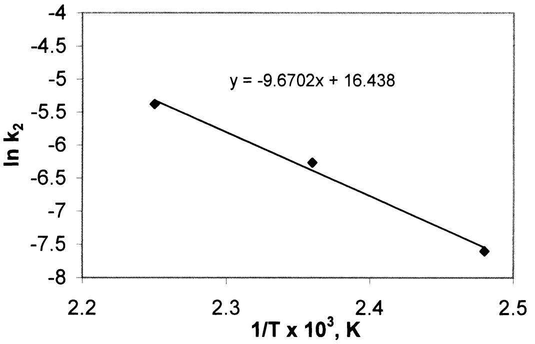


Fig. 6. Arrhenius plot.

in Fig. 5. The equation fits the data quite well. From the slope of this plot, the value of the reaction rate constant k_2 at 150°C was found to be $0.016\,\mathrm{cm}^6\,\mathrm{gmol}^{-1}\,\mathrm{gcat}^{-1}\,\mathrm{s}^{-1}$. Similar plots were made for different temperatures as shown; values were calculated at other temperatures and the Arrhenius plots of $\ln k_2$ vs T^{-1} (Fig. 6) were made to get the apparent energy of activation as 19.34 kcal/mol, thereby also suggesting the reaction was intrinsically kinetically controlled.

6. Conclusions

The alkylation of hydroquinone was studied with MTBE and *tert*-butanol as alkylating agents with a variety of catalysts amongst which 20% (w/w) DTP on K10 (DTP/K-10) was found to be the best catalyst. The rate of alkylation of hydroquinone with MTBE was much faster than that with *tert*-butanol. The reaction mechanism involves weak adsorption of MTBE on the catalyst followed by surface reaction with hydroquinone leading to a typical second order kinetics at a fixed catalyst loading.

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