Synthesis of Hydroquinone Monomethyl Ether from Hydroquinone and Methanol over Heteropolyacids Supported on Clay: Kinetics and Mechanism

Ganapati D. Yadav,* Salim A. R. K. Deshmukh, and Navinchandra S. Asthana

Department of Chemical Engineering, University Institute of Chemical Technology, University of Mumbai, Matunga, MUMBAI-400 019, India

Hydroquinone mono methyl ether (HMME) is industrially a very important anti-oxidant, produced by environmentally undesirable routes. In the current studies, HMME was synthesized from hydroquinone and methanol catalyzed by various solid acids using montmorillonite clay (K10) as a support with different loadings of dodecatungstophosphoric acid (DTP), $AlCl_3$, $FeCl_3$, and $ZnCl_2$. Among these, 40% DTP/K10 with benzoquinone as cocatalyst was the most active and selective. The reaction mechanism suggests that benzoquinone couples with protonated methanol on the catalyst site to yield an intermediate, which reacts with hydroquinone adjacent to the site. The surface reaction between the intermediate and chemisorbed hydroquinone controls the overall rate of reaction. There is 100% selectivity toward HMME. The experimental data are well correlated with the model. Excess of methanol favors the formation of HMME.

Introduction

Hydroquinone mono methyl ether (HMME), which is also called *p*-hydroxyanisole (PHA), is useful as a polymerization inhibitor for acrylic compounds; as an antioxidant for edible oils and greases; as a stabilizer for photo sensitive materials, polyesters, intermediate dyes, agrochemicals, and drugs; as a lubricating additive for high-temperature gas turbine engine oils; as an inhibitor of retrovirus and therapy of aids; and also as a synthetic intermediate. The principal route for the preparation of HMME is by the reaction of hydroquinone with methanol in the presence of acid catalysts with a suitable cocatalyst,[1−3] but no satisfactory route has yet been developed. In this reaction, typically homogeneous acids are used as catalysts, which pose problems of separation and reuse of the acids or treatment of acidic effluent. Solid acids are being used as substitutes for liquid acids for a number of fine chemical processes, and zeolites have been the favorite.[4−6] Several inorganic oxides, mixed oxides, including alumina, silica, titania, zirconia, and zeolites, and clays have been used as both supports and solid acid catalysts. Clay structure collapses at high temperatures and has to be stabilized.[4,5,7] Various modifications of clay such as acid activation, pillaring, etc. alter the structure of clay and thereby affect the acidity. The thermal stability of clays is increased by pillaring. Ion-exchange resins form a special class of catalysts. Heteropoly acids (HPA) are employed as homogeneous or heterogeneous catalysts, having both acid and redox properties.[7−16]

The importance of sulfated zirconia as an alternative to zeolites has been brought out in our laboratory in a number of commercially significant reactions.[15−28] The synergism of heteropolyacids (HPA) with acid treated clays (e.g., K10, Filtrol-24) was brought out by us for the first time in our pioneering paper,[29] and several

reactions using dodecatunstophosphoric acid (DTP)/K10 were studied from mechanistic and kinetic viewpoints.[40] These catalysts are reusable and have better activity than clay supported Lewis acids.[41,42] Besides, $Cs_{2.5}H_{0.5}$-$PW_{12}O_{40}$/K10 was found to be a superior catalyst.[43−47] HPA on hexagonal mesoporous silica is also a better acylating catalyst than zeolites.[48]

There is a dearth of published literature on the use of solid acids in the synthesis of HMME. Therefore, the current work was undertaken to evaluate the performance of different clay based solid acids to synthesize HMME by the reaction of hydroquinone and methanol, which would lead to high activity and selectivity for HMME. Heteropoly acids supported on clay were considered as possible catalysts. Besides, the kinetic modeling of the reaction was also targeted. This paper gives the details of these findings.

Experimental Section

Chemicals and Catalysts. Hydroquinone (HQ), benzoquinone, methanol, dodecatungstophosphoric acid (DTP), $AlCl_3$, $ZnCl_2$, and 1,4-dioxane were obtained from M/s s.d. Fine Chemicals Pvt. Ltd., Mumbai, India. K10 montmorillonite clay was obtained from Fluka. 20% w/w $AlCl_3$−$ZnCl_2$ (1:1)/K10, 40% w/w DTP/K10 clay was prepared as per the procedure developed in this laboratory[29,37] and fully characterized as reported elsewhere.[30,31] All other chemicals were pure grade laboratory reagents procured from M/s s.d. Fine Chemicals Pvt Ltd.

Reaction Procedure. All experiments were carried out in a Parr autoclave of 10^{-4} m^3 capacity. Typical experiments were performed with 2.7×10^{-2} mol hydroquinone, 1.08 mol methanol, and 2.78×10^{-3} mol benzoquinone as cocatalyst keeping the total volume of the reaction mixture as 70 cm^3 with 1,4-dioxane as a solvent at a catalyst loading of 0.02 g/cm^3 at 473 K. The speed of agitation was maintained at 16.67 rps. Sampling was done periodically up to 900 s at shorter intervals of time and thereafter at longer intervals up

* To whom correspondence should be addressed. Tel.: (91-22) 2410-2121. Fax: (91-22) 2414-5614. E-mail: gdyadav@yahoo.com; gdyadav@udct.org.

Table 1. Dynamic Adsorption Studies in a Slurry Reactor[a]

no.	adsorbate	initial concentration (mol/cm^3)	solvent	K_{ad} (cm^3/mol)	average value K_{ad} (cm^3/mol)
1	methanol	3.5×10^{-3}	1,4-dioxane	1.298×10^3	1.35×10^3
2	benzoquinone	3.92×10^{-5}	1,4-dioxane	1.16×10^5	7.34×10^4
3	hydroquinone	3.85×10^{-4}	1,4-dioxane	2×10^3	2.85×10^3
4	HMME	1.44×10^{-4}	1,4-dioxane	5×10^3	6.05×10^3
5	water	1.44×10^{-4}	1,4-dioxane	1.15×10^3	1.15×10^3
6	methanol	3.5×10^{-3}	none	3.60×10^2	
	benzoquinone	3.92×10^{-5}		1×10^5	
7	methanol	7.14×10^{-4}	none	2.4×10^3	
	HMME	1.44×10^{-4}		7.1×10^3	
8	hydroquinone	2.857×10^{-4}	none	3.7×10^3	
	benzoquinone	2.857×10^{-4}		4.2×10^3	
9	methanol	7.14×10^{-4}	none	2.35×10^3	
	water	1.44×10^{-4}		0.90×10^3	

[a] Catalyst = 40% w/w DTP/K10 clay, catalyst loading = 0.02 g/cm^3, volume of liquid phase = 70 cm^3, temperature = 65 °C.

to 14 400 s and analyzed by HPLC. The overall reaction is depicted below:
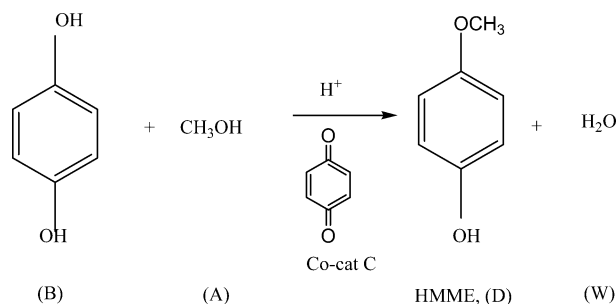
Adsorption Experiments. The reaction did not proceed unless benzoquinone was added to the reaction mixture. It was therefore essential to conduct independent adsorption studies of all components of the reaction mixture. Adsorption of hydroquinone, methanol, HMME, and benzoquinone as single components from 1,4-dioxane as the solvent on DTP/K10 as the catalyst was studied at 65 °C by using the dynamic adsorption technique.[49] Mixtures of binary components such as methanol and benzoquinone, methanol and HMME, and hydroquinone and benzoquinone from 1,4-dioxane were also used for the adsorption studies at 65 °C (Table 1). The assembly used for the adsorption experiments consisted of a flat-bottomed cylindrical glass vessel of 100 mL capacity equipped with four baffles, a pitched-turbine stirrer, and a condenser. The assembly was kept in a thermostatic oil bath at the desired temperature and mechanically agitated with an electric motor. The mass was allowed to reach 65 °C, and agitation was then commenced at 16.67 rps. Clear samples were withdrawn periodically for analysis. The concentration of the particular adsorbate in the liquid phase was noted at the start of the run, and then periodic samples were withdrawn and analyzed by HPLC. The concentration profile of the adsorbate was monitored with time, until there was no more adsorption, which was confirmed by taking samples for further 2 h. The initial and final values of concentration of the adsorbate in the liquid phase were used to calculate the adsorption equilibrium constants. Two types of experiments were done. Individual component, with known amount, was taken in a suitable nonadsorbing solvent (1,4-dioxane) and mixed with a known quantity of catalyst, whereas in the case of nonreacting mixtures, no solvent was used; the data are presented in Table 1. These studies were helpful in getting the relative rates of adsorption and also the adsorption constant. It was found that benzoquinone,

the cocatalyst, was strongly adsorbed, by 2 more orders of magnitude than all other species.

Analysis. Analysis of the reaction mixture was done by HPLC (model TOSHO) with the following conditions: Column Novopack RP 18; mobile phase, methanol:water (50:50); flow rate, 1.67×10^{-8} m^3/s; detector wavelength, 293 nm. Identification of products was done by matching the retention time of products to the authentic compounds.

Results and Discussion

Efficacies of Different Catalysts. A variety of clay supported catalysts were employed in this reaction: 40% w/w DTP/K10, 20% w/w AlCl$_3$−FeCl$_3$ (1:1)/K10, 20% w/w ZnCl$_2$/K10. These catalysts were chosen on the basis of our past experience in etherification reactions.[30−33,38−40] Preliminary experiments were conducted by taking only hydroquinone, methanol, and the solid acids at 473 K and 3.039 MPa autogenous pressure. It was observed that HMME was not formed even after 14 400 s. It was found that the addition of a cocatalyst was necessary for initiation of the reaction, and therefore 2.78×10^{-3} mol benzoquinone was added as a cocatalyst to the standard reaction mixture. In fact, the effect of loading of DTP on K10 was studied initially. Among all catalysts, 40% w/w DTP/K10 was the only catalyst with benzoquinone as cocatalyst that was effective. The main product of formation was monoalkylated hydroquinone, because methanol was taken in far excess molar quantity vis-a-vis hydroquinone. No diether of hydroquinone was formed, and the selectivity of hydroquinone mono methyl ether was 100%. Even with 40% w/w DTP/K10, no reaction took place in the absence of the cocatalyst benzoquinone. In our earlier studies, we have found that DTP/K10 was a novel catalyst with very high acidity in comparison with several others for etherification of *tert*-butyl alcohol,[33,39,40] and phenethyl alcohol[31] with methanol, and in the case of etherification of hydroquinone with methanol it was essential to have very high acidities. The surface area of K10 clay is 230 m^2/g with pore size ranging in meso- and microporous regions. The loading of DTP on K10 clay imparts it more of Bronsted acidity, and the surface area is reduced drastically to 107 m^2/g. This is essential for the reaction, and only the O-alkylated product of hydroquinone is formed.

The conversion of hydroquinone is much faster during the initial 900 s, and thereafter the rate decreased progressively. Thus, the effect of various parameters on the rate of reaction and hence conversion were studied with 40% w/w DTP/K10 under otherwise similar conditions for the first 900 s. Typical conversion profiles are
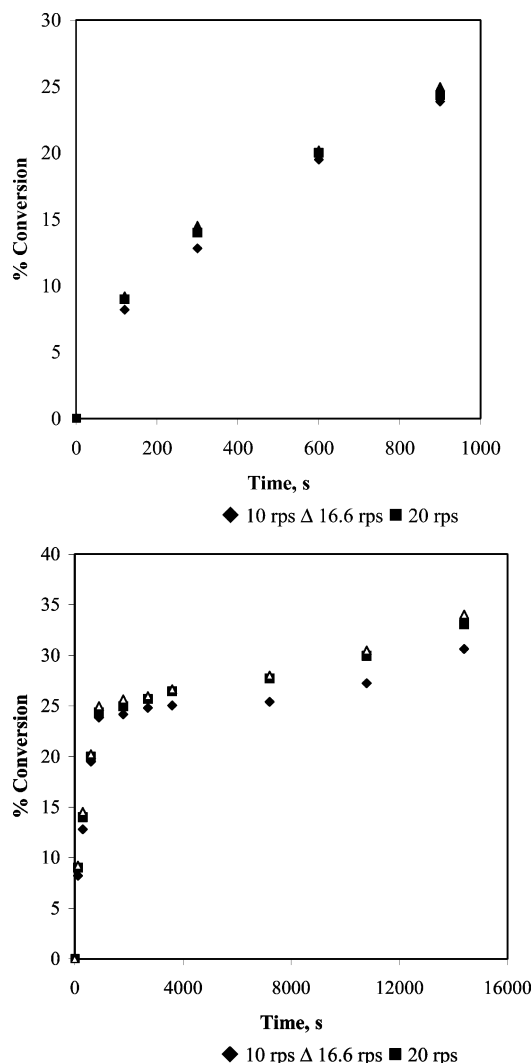
Figure 1. (a) Effect of speed of agitation up to 900 s: catalyst loading 0.02 g/cm^3 of hydroquinone (HQ), 2.7×10^{-2} mol of catalyst DTP/K10, mole ratio 1:40, temperature 473 K, benzoquinone 10% w/w of HQ. (b) Effect of speed of agitation up to 14 400 s: catalyst loading 0.02 g/cm^3 of hydroquinone (HQ), 2.7×10^{-2} mol of catalyst DTP/K10, mole ratio 1:40, temperature 473 K, benzoquinone 10% w/w of HQ.

shown in Figure 1a and b at different speeds of agitation and will be discussed later.

Characterization of DTP/K10. DTP/K10 was reported for the first time as a novel catalyst by our laboratory. It has already been fully characterized by us,[29] and a brief summery is provided here. The surface areas of catalysts measured by nitrogen BET method for K10 montmorillonite and DTP/K10 were found to be 230 and 107 m^2/g, respectively. The pore volume is 0.36 cm^3/g, and the average pore diameter is 6.4 nm. It contains mainly Bronsted acidic sites. The pore volume of DTP/K10 was 0.28 cm^3/g, and the average pore diameter was 7.0 nm.

Because both the K10 support and the catalysts were pretreated in a similar way prior to analysis, the reduction in surface area of DTP/K10 may be due to the blockage of smaller pores by active species. It appears the active spices are held in 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 60 μm. The XRD studies of DTP/K10 had indicated that in the impregnation process, the clay has lost some of its crystallinty as 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 proton, which comes by way of heteropoly acid impregnation and may play a role on account of easy availability for the exchange reaction. In the case of DTP/K10, there are a lot of disperse particles on the surface of the support K10 as revealed by the SEM photograph.

FTIR studies of K10 showed that there was Si−O and Si−O−al linkage and the OH groups are bonded to the al atoms, whereas in DTO/K10 the presence of H$_3$O$^+$ (Bronsted acidity) and linkage of phosphorus was indicated.

Adsorption Studies. Table 1 lists the conditions under which adsorption of various components was carried out. It is seen that benzoquinone is very strongly adsorbed (almost 2 orders of magnitude) on the catalyst site in comparison with others. The product HMME is also fairly strongly adsorbed, whereas methanol is weakly adsorbed. The reason that the reaction did not proceed without benzoquinone could be established due to the fact that benzoquinone forms a carbocation with the acidic sites and then it initiates the reaction. At the same time, when a sufficient amount of HMME is formed, it reduces the number of sites available for reaction and the rate reaches a plateau. These observations were helpful in building a kinetic model.

Effect of Speed of Agitation. The influence of external mass transfer resistance was verified for the transfer of the limiting reactant hydroquinone to the external surface of the catalyst particle. Thus, the effect of speed of agitation was studied at the temperature of 473 K for a catalyst loading of 0.02 g/cm^3 (Figure 1a). The speed of agitation was varied from 10 to 20 rps, and it was found that the conversion of hydroquinone and the product distribution was similar in all of the cases. A theoretical calculation was also done to ascertain the magnitude of external mass transfer rates and reaction rate as discussed in our earlier work.[39,40] The bulk liquid-phase diffusivities of reactants were obtained by using the Wilke−Chang equation and solid−liquid mass transfer coefficients by using the Sherwood number correlation.[49] The mass transfer rates for hydroquinone and methanol to the external surface of the catalyst were calculated and compared to the observed rate of reaction for standard reaction conditions. The mass transfer rates were in 3−4 orders of magnitude in excess over observed rates of reaction. Thus, the external resistance to mass transfer was absent. Further experiments were conducted at 16.67 rps.

Effect of Catalyst Loading. The catalyst loading was varied from 0.005 to 0.02 g/cm^3 (Figure 2). It was found that the yield of HMME increased with an increase of the catalyst loading up to 0.02 g/cm^3, beyond which no substantial effect was found. The rate of alkylation was very slow with 0.005 g/cm^3 catalyst loading and only 13% conversion of hydroquinone was obtained. The initial rates of reaction were found to be linear in catalyst loading in the range of 0.005−0.02 g/cm^3, which is due to the proportional number of active sites. When the loading was increased from 0.02 to 0.04 g/cm^3, the rate of reaction was almost similar and 34% conversion of HQ with 100% selectivity of HMME was
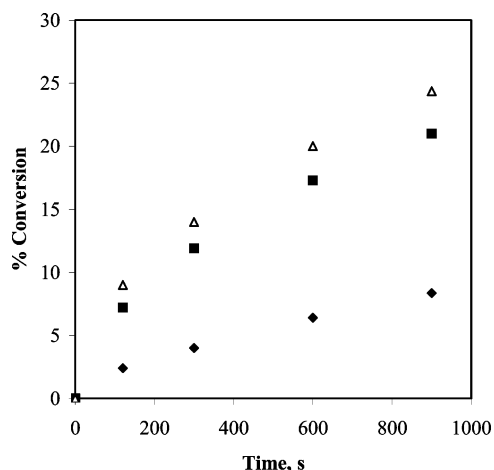
Figure 2. Effect of catalyst loading hydroquinone (HQ), 2.7×10^{-2} mol of catalyst DTP/K10, mole ratio 1:40, temperature 473 K, speed 16.6 rps, benzoquinone 10% w/w of HQ.
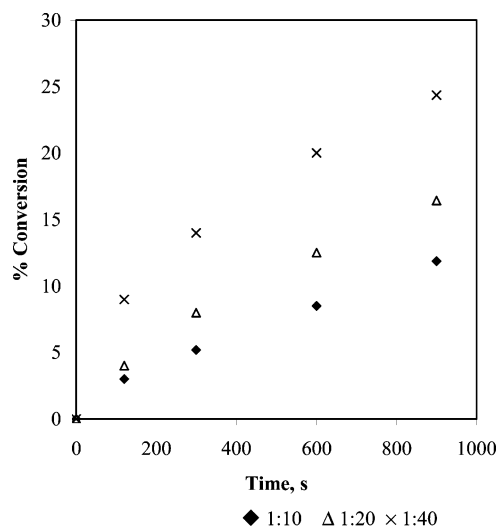

◆ 1:10   △ 1:20   × 1:40

Figure 3. Effect of mole ratio catalyst loading 0.02 g/cm^3 of hydroquinone (HQ), 2.7×10^{-2} mol of catalyst DTP/K10, temperature 473 K, speed 16.6 rps.

◆ 0.0079 x10^{-3} mol/cm^3 ■ 0.019 x10^{-3} mol/cm^3 O 0.119 x10^{-3} mol/cm^3
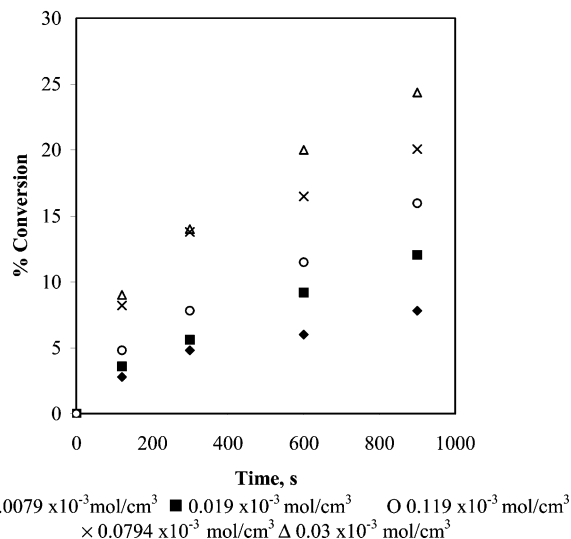× 0.0794 x10^{-3} mol/cm^3 △ 0.03 x10^{-3} mol/cm^3

Figure 4. Effect of benzoquinone catalyst loading 0.02 g/cm^3 of hydroquinone (HQ), 2.7×10^{-2} mol of catalyst DTP/K10, mole ratio 1:40, temperature 473 K, speed 16.6 rps.

obtained in both of the cases. This was because of the fact that beyond a certain loading, there exists an excess of catalyst sites than is actually required by the reactant molecules, and hence additional catalyst does not increase the rate of reaction.

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.

(i) If $C_{wp} = r_{obs}\rho_p R_P{}^2/D_e C_{AS} \gg 1$, then the reaction is limited by severe internal diffusional resistance. (ii) If $C_{wp} \ll 1$, then the reaction is intrinsically kinetically controlled.

The effective diffusivity of hydroquinone (D_{e-A}) inside the pores of the catalyst was obtained from the bulk diffusivity (D_{AB}), porosity (ϵ), and tortuosity (τ) as 2.5×10^{-5} cm^2/s, where $D_{e-A} = D_{AB}\epsilon/\tau$. In the present case, the value of C_{wp} was calculated as 2.53×10^{-4} for the initial observed rate, which is much less than 1, and therefore the reaction is intrinsically kinetically controlled. 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.

Effect of Mole Ratio. It was found that excess of methanol present in the reaction favored the formation of monoalkyl derivatives. When the mole ratio of hydroquinone to methanol was increased from 1:10 to 20:1 to 1:40, the conversion of hydroquinone was found to increase (Figure 3). The rate of reaction is a strong function of concentration of hydroquinone and methanol. Besides, there was no formation of any dimethyl ether due to dehydration of methanol. The selectivity to HMME was 100% at all mole ratios. It was also found that in the absence of benzoquinone, there was no formation of HMME at all mole ratios.

Effect of Benzoquinone. Because benzoquinone is essential as a cocatalyst in the etherification reaction, the effect of benzoquinone concentration was studied from 7.94×10^{-6} to 1.19×10^{-4} mol/cm^3. It was observed that the conversion of hydroquinone increased with an increase in concentration of benzoquinone up to 3.968×10^{-5} mol/cm^3, beyond which the conversion of hydroquinone decreased (Figure 4). This was a conse-

quence of the poisoning of the catalyst due to excessive adsorption of benzoquinone, because benzoquinone was found to adsorb strongly on DTP/K10. Further experiments were carried out with 3.968×10^{-5} mol/cm^3 loading of benzoquinone, which gave maximum conversion under otherwise similar conditions.

Effect of Temperature. Temperature plays an important role in alkylation of hydroquinone. It shows that with an increase in temperature, the rate of reaction also increases. The reactions were studied for 14 400 s in all cases. However, for kinetic measurements, data were used up to 900 s (Figure 5). At low temperature (443 K), the conversion of hydroquinone was 24% with 100% selectivity for HMME after 14 400 s (point not shown). It was found that no dialkylated product was found even when the temperature was increased from 443 to 483 K. This is because of the presence of excess methanol in the reaction mixture. A maximum conversion of 39% was obtained at 483 K after 14 400 s under otherwise similar conditions (point not shown). These studies also indicated that the reaction is intrinsically kinetically controlled, and this is discussed after the development of the kinetic model.

Scheme 1. Mechanism of Etherification of Hydroquinone with Methanol
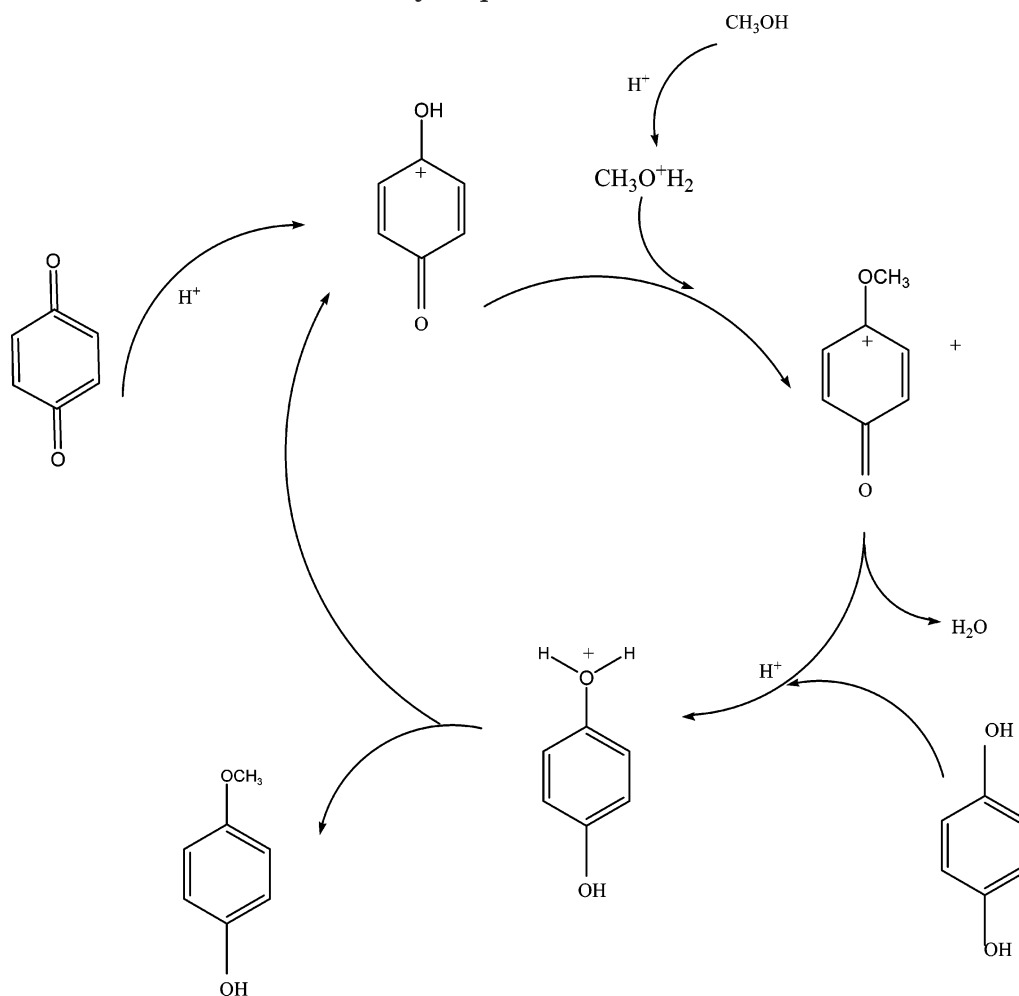
Reusability of Catalyst. Reusability of DTP/K10 was tested by conducting three runs. After each run, both of the catalysts were thoroughly washed with warm methanol and dried at 393 K for 7200 s prior to reuse. In the presence of DTP/K10, the conversion of hydroquinone was reduced to an extent of 33% from the first run to the third run, without any change in the

selectivity of HMME. There were some losses during filtration, washing, and drying, and no make-up catalyst was added to the system. The reduction is thus marginal. In another experiment, make-up catalyst was added to find that the catalyst activity was almost the same within experimental error. This would suggest that the catalyst is stable, without any poisoning and reusable.

Establishment of Kinetics. The above experiments demonstrated that benzoquinone (C) is essential as a cocatalyst for the reaction to proceed. Scheme 1 depicts the catalytic cycle. This mechanism is based on the Langmuir−Hinshelwood−Hougen−Watson (LHHW) model involving several steps. Benzoquinone interacts with the acidic site (designated by a general proton H^+) (S) to give a protonated chemisorbed species (CS), and methanol is also protonated on an adjacent site.
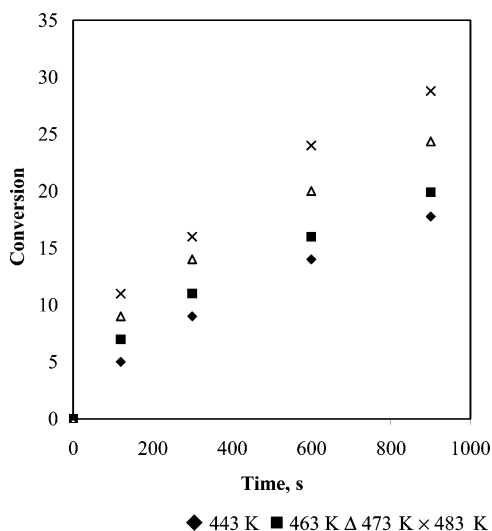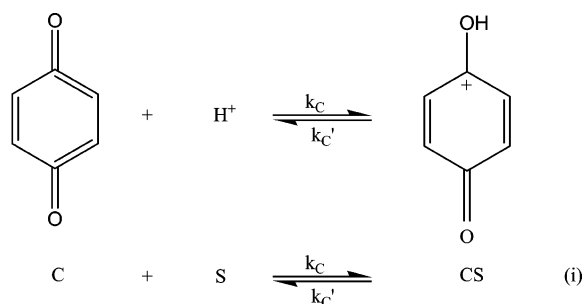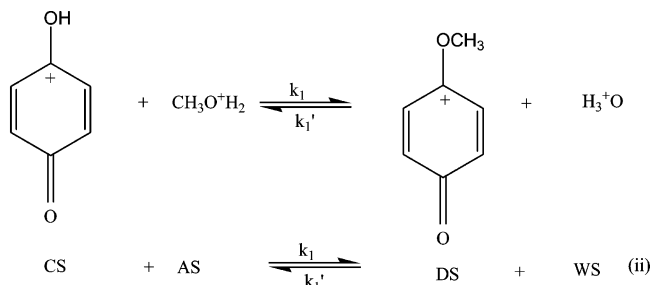

Figure 5. Effect of temperature catalyst loading 0.02 g/m³ of hydroquinone (HQ), 2.7×10^{-2} mol of catalyst DTP/K10, mole ratio 1:40, speed 16.6 rps, benzoquinone 10% w/w of HQ.

$$C + S \underset{k_C'}{\overset{k_C}{\rightleftharpoons}} CS \qquad (i)$$

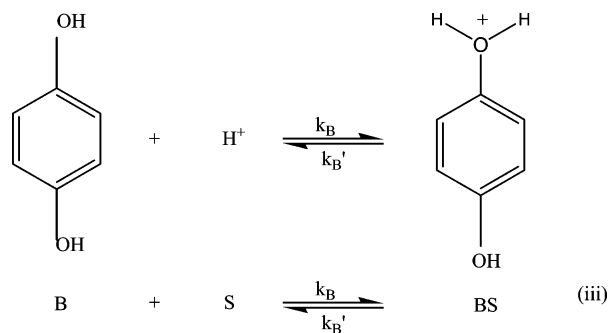The rate of adsorption of C is given by

$$r_C = k_C C_C C_S - k'_C C_{CS} \qquad (1)$$

The chemisorbed methanol (AS) reacts with CS as shown below to give another species DS and WS according to LHHW model.

$$CS \ + \ AS \ \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \ DS \ + \ WS \qquad (ii)$$

This surface reaction is given by

$$r_1 = k_1 C_{CS} C_{AS} - k'_1 C_{DS} C_{WS} \qquad (2)$$

Hydroquinone is chemisorbed as given below:

$$B \ + \ S \ \underset{k_B'}{\overset{k_B}{\rightleftharpoons}} \ BS \qquad (iii)$$

The rate of chemisorption of hydroquinone (B) is given by

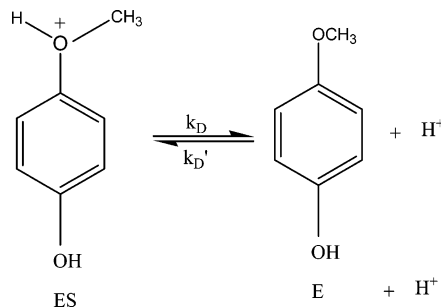$$r_B = k_B C_B C_S - k'_B C_{BS} \qquad (3)$$

The next step is the reaction between DS and BS to produce the product ES, and the cocatalyst is released as CS. This reaction is rate determining, and hence only the forward rate is shown:

$$DS \ + \ BS \ \xrightarrow{k_{SR}} \ ES \ + \ CS$$
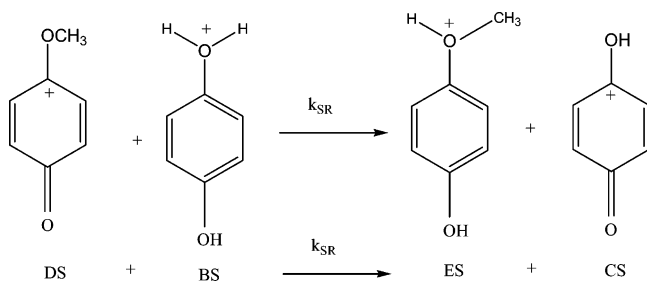
Also,

$$r_{SR} = k_{SR} C_{DS} C_{BS} \qquad (4)$$

The desorption of product ES proceeds according to the following:

$$ES \qquad\qquad E \ + \ H^+$$

Also,

$$r_D = k_D C_{ES} - k'_D C_E C_S \qquad (5)$$

The site balance is given by

$$C_t = C_S + C_{CS} + C_{DS} + C_{BS} + C_{ES} + C_{AS} + C_{WS} \qquad (6)$$

Considering eq 4 as a rate-determining step and subsequently all other steps being in equilibrium, we obtain the adsorption equilibrium constants as follows.
From eq 1:

$$K_C = \frac{C_{CS}}{C_C C_S} \qquad (7)$$

From eq 2:

$$K_1 = \frac{C_{DS} C_{WS}}{C_{CS} C_{AS}} \qquad (8)$$

From eq 3:

$$K_B = \frac{C_{BS}}{C_B C_S} \qquad (9)$$

From eq 5:

$$K_{D'} = \frac{C_{ES}}{C_E C_S} \qquad (10)$$

By putting the values of eqs 7−10 in eq 6, we obtain

$$C_t = C_S + K_C C_C C_S + \frac{K_1 K_C C_C K_A C_A C_S}{K_W C_W} + K_B C_B C_S + \\ K_{D'} C_E C_S + K_A C_A + K_W C_W \qquad (11)$$

Therefore, the concentration of vacant sites could be written as

$$C_S = C_t \Big/ \Big(1 + K_C C_C + \frac{K_1 K_C C_C K_A C_A}{K_W C_W} + K_B C_B + \\ K_{D'} C_E + K_A C_A + K_W C_W \Big) \qquad (12)$$
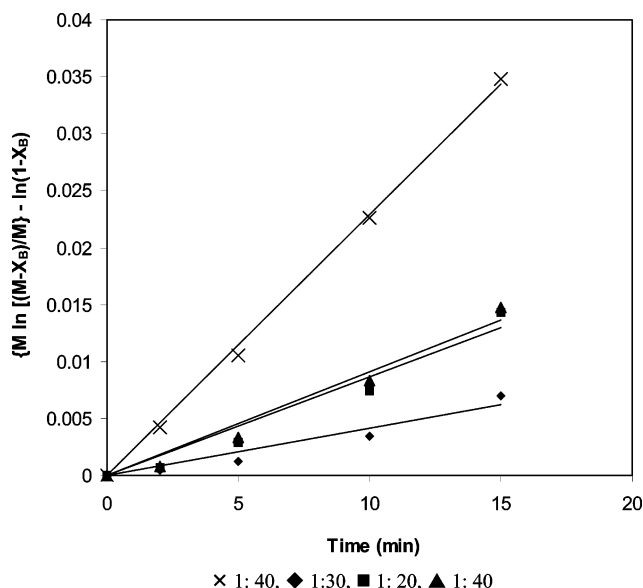
Figure 6. Plot of $\{M \ln[(M - X_B)/M]\} - \ln(1 - X_B)$ versus t for $M > 1$ for different mole ratios.

The incorporation of the various adsorption equilibrium constants shows that the terms in denominator are equal to unity. Further, benzoquinone is very strongly adsorbed on the catalyst and is used in a very small concentration, and hence all benzoquinone is totally adsorbed.

Thus, $C_{CS} \cong C_C$ and $C_S \approx C$ and in terms of catalyst loading w (g/cm^3), $C_S = k_t w$.

From eq 4, we get:

$$r_{SR} = k_{SR} \frac{K_1 C_{CS} K_A C_A K_B C_B C_S}{K_W C_W} \quad (13)$$

$$r_{SR} = k_{SR} \frac{K_1 K_t K_B K_A C_C C_A C_B w}{C_W} = k' \frac{C_C C_A C_B}{C_W} \quad (14)$$

the rate of reaction of hydroquinone (B), which was the limiting reactant,

$$r_{SR} = -\frac{dC_B}{dt} = C_{Bo} \frac{dX_B}{dt} = k' \frac{C_C C_A C_B}{C_W} \quad (15)$$

in terms of X_B, factional conversion of B, and initial mole ratio M

$$C_B = C_{B0}(1 - X_B); \quad C_A = C_{B0}(M - X_B);$$

$$C_W = C_{B0} X_B; \quad C_E = C_{B0} X_B; \quad M = \frac{C_{A0}}{C_{B0}} \quad (16)$$

Therefore,

$$\frac{dX_B}{dt} = k' \frac{(1 - X_B) \cdot (M - X_B)}{X_B} \cdot w \quad (17)$$

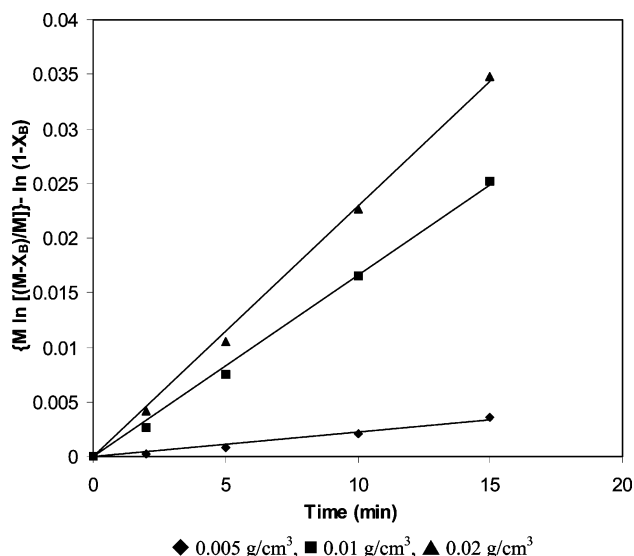Separation of variables and integration leads to the

$\blacklozenge$ 0.005 g/cm^3, $\blacksquare$ 0.01 g/cm^3, $\blacktriangle$ 0.02 g/cm^3

Figure 7. Plot of $\{M \ln[(M - X_B)/M]\} - \ln(1 - X_B)$ versus t for $M = 40$ for different catalyst loading.

$\times$ 210°C, $\blacktriangle$ 200°C, $\blacksquare$ 190°C, $\blacklozenge$ 170°C
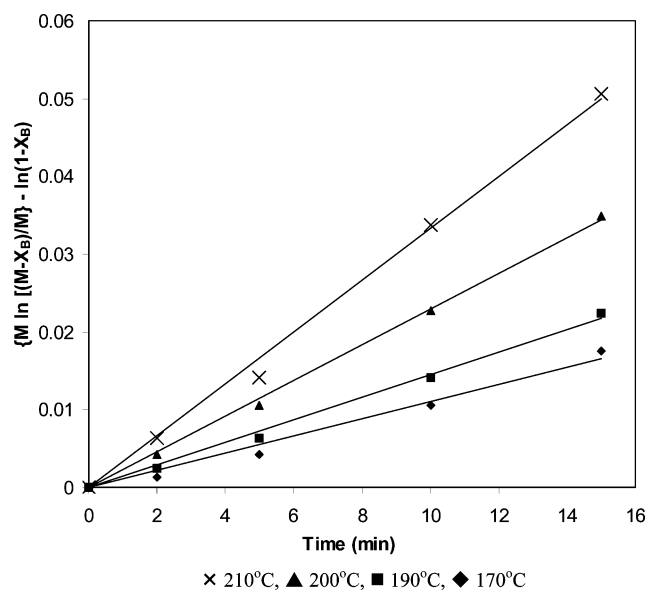
Figure 8. Plot of $\{M \ln[(M - X_B)/M]\} - \ln(1 - X_B)$ versus t for $M = 40$ at different temperatures.

following: (i) when $M \neq 1$,

$$M \ln \left\{ \frac{(M - X_B)}{M} \right\} - \ln(1 - X_B) = (M - 1)k'wt \quad (18)$$

(ii) when $M = 1$,

$$\ln(1 - X_B) + \frac{X_B}{(1 - X_B)} = k'wt \quad (19)$$

Validation of the Theory. Thus, the left-hand side (LHS) of eq 18 is plotted against time for different values of M (Figure 6), for different catalyst loadings, w (Figure 7) and different temperatures for the same value of M (Figure 8), which all show that the data fit very well. This proves that the theory is valid. In the current studies, no equimolar quantities of methanol and hydroquinone were used because the rates were low and appreciable conversions were obtained when M was very high.
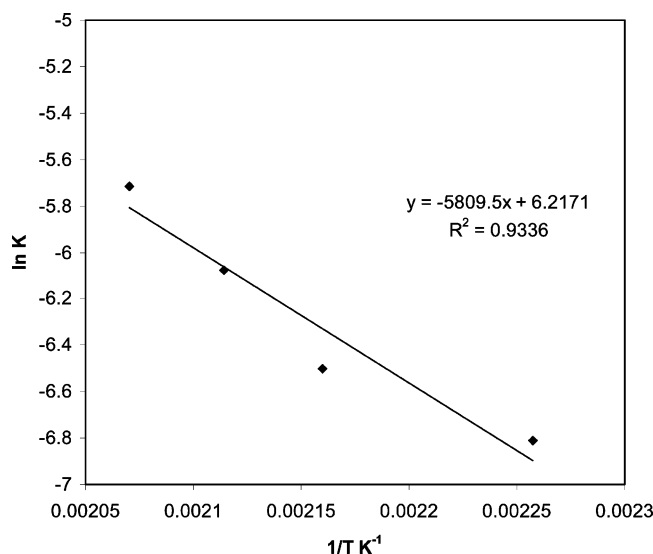
Figure 9. Arrhenius plot.

Indeed, the values of k' at different temperatures were used to make the Arrhenius plot (Figure 9). The apparent activation energy is 11.50 kcal/mol, which is also suggestive that the reaction is intrinsically kinetically controlled.

Conclusions

Hydroquinone mono methyl ether (HMME) is a very valuable chemical with several applications. The etherification of hydroquinone with methanol was examined by using various catalysts based on clay supports. A synergistic combination of dodecatungstophosphoric acid (DTP) supported on K10 clay was found to be the best among all studied. 40% w/w DTP/K10 clay gave the best activity of all other catalysts used only in the presence of a cocatalyst benzoquinone in the liquid phase. There is 100% selectivity to HMME. The reaction mechanism that follows Langmuir−Hinshelwood−Hougen−Watson kinetics suggests that benzoquinone is protonated, which couples with protonated methanol on the catalyst site to yield an intermediate complex that is responsible for the initiation of the reaction. This intermediate complex reacts with hydroquinone protonated on the adjacent to yield the product hydroquinone mono methyl ether, which is the rate-controlling step. Excess of methanol favors the formation of hydroquinone mono methyl ether. Adsorption studies were also conducted to determine the various adsorption equilibrium constant. Benzoquinone is strongly adsorbed, and a certain critical concentration, without affecting the adsorption of others, is required for the reaction to proceed. The experimental data were well correlated with the model.

Acknowledgment

Nomenclature

A = hydroquinone
B = methanol
C = benzoquinone

AS, BS, ... = chemisorbed species A, B, etc.
C_A, C_B, C_{AS}, C_{BS} = concentrations of A,B, AS, BS, etc. (mol/cm^3)
C_{A0}, C_{B0}, C_{C0} = initial concentrations of A, B, and C (mol/cm^3)
C_S, C_t = concentration of vacant sites and total sites, respectively (mol/g-cat)
C_{wp} = Wiesz−Prater parameter
K_A, K_B, K_C, K_D = surface reaction rate constants
k' = overall reaction rate constant
M = mol ratio of methanol to hydroquinone
r = reaction rate, mol (g-cat s)$^{-1}$
r_{obs} = observed rate of reaction, mol (g-cat s)$^{-1}$
R_P = particle radius (cm)
ρ_p = particle density (g/cm^3)
t = time (s)
w = solid loading per unit liquid-phase volume (g/cm^3)
X_B = fractional conversion of B

Subscripts

0 = initial conditions

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