

Chemoselective catalysis by sulphated zirconia in *O*-alkylation of guaiacol with cyclohexene

Ganapati D. Yadav*, Ganesh S. Pathre

Department of Chemical Engineering, University Institute of Chemical Technology (UICT), University of Mumbai, Matunga, Mumbai 400019, India

Received 30 April 2005; received in revised form 31 July 2005; accepted 1 August 2005

Available online 21 September 2005

Abstract

Alkylation of guaiacol(2-methoxyphenol) with cyclohexene gives both *O*- and *C*-alkylated products. The *O*-alkylated product 1-cyclohexyloxy-2-methoxybenzene(cyclohexyl-2-methoxyphenyl ether) is used as a perfumery compound. The current work was aimed at achieving maximum selectivity for this product by using an active catalyst with minimum separation cost. It covers the use of a variety of solid acid catalysts such as sulphated zirconia, Amberlyst-15, Filtrol-24, Indion-130, 20% (w/w) dodecatungstophosphoric acid supported on K-10 clay (DTP/K-10) and 20% (w/w) cesium-modified dodecatungstophosphoric acid supported over K-10 clay ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$). Sulphated zirconia was found to be the best catalyst to achieve maximum selectivity for the ether. The *O*-alkylation versus *C*-alkylation selectivity was not only highly temperature sensitive but also the pore size and nature of acidic sites also played an important role. The reaction was carried out without using solvent. No oligomerisation of cyclohexene was formed over the temperature range employed. A suitable kinetic model is proposed and validated.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Friedel–Crafts alkylation; Solid superacids; Guaiacol; Cyclohexene; Sulphated zirconia; Benign process; Amberlyst-15; Heteropolyacids; Clay; 1-Cyclohexyloxy-2-methoxybenzene; Cyclohexyl-2-methoxyphenyl ether

1. Introduction

Friedel–Crafts alkylations are ubiquitous and catalysed by acids. Of late, the use of solid acids over liquid acids is preferred to develop green and clean processes. Friedel–Crafts alkylation of phenols, using solid acids, with a variety alkylating agents such as alkenes, alkanols, ethers and alkyl halides gives both *O*- and *C*-alkylated products. The formation of these products is dependent on several factors such as temperature, pore size and nature of active sites present in catalyst, alkylating agent and solvent [1–6].

Alkylation of guaiacol(2-methoxyphenol) with cyclohexene yields *O*- and *C*-alkylated products, all of which have commercial value. The *O*-alkylated product (cyclohexyl-2-methoxyphenyl ether) is a promising perfume. Hence, it is desirable to produce it selectively. Furthermore, since the selective hydrogenation of benzene to cyclohexene has been commercialized, cyclohexene will gain considerable value as a starting

material for many industrial chemicals like cyclohexanol, cyclohexanone, cyclohexylphenols, cyclohexyl esters and ethers.

No detailed studies have been apparently made on the alkylation of guaiacol with cyclohexene. Most research is in the patented form. A yield of 53% of 4-cyclohexyl guaiacol is reported from the reaction of guaiacol and cyclohexene with 98% H_2SO_4 as catalyst [7]. Use of KU catex cation exchange resin [8] and ZnCl_2 –HCl solution as catalysts is reported [9]. Alkylation is reported with cyclohexanol as an alkylating agent [10,11]. Sulphated zirconia holds great promise in a number of reactions of industrial importance due to its superacidity, low cost and high thermal stability [12–19]. Reaction between *p*-cresol and cyclohexene was reported with sulphated zirconia as a catalyst with maximum selectivity for *O*-alkylation [20]. Recently Yadav and Kumar [21] studied alkylation of phenol with cyclohexene using 20% (w/w) dodecatungstophosphoric acid (DTP)/K-10 and sulphated zirconia (S-ZrO_2) at lower temperature and reported very good selectivity for the ether by both the catalysts. It appears that synergistic effect of both Lewis and Brønsted acids gives *O*-alkylation selectively. Apparently no systematic study has been carried out on the alkylation of guaiacol with cyclohexene and there does not appear much evidence

* Corresponding author. Tel.: +91 22 2410 2121/2414 5616;

fax: +91 22 2410 2121/2414 5614.

E-mail addresses: gdyadav@yahoo.com, gdyadav@udct.org (G.D. Yadav).

Nomenclature

A	reactant species A, cyclohexene
B	reactant species B, guaiacol
AS, BS, CS, D _i S	chemisorbed species A, B, C, D _i
C _A	concentration of A (kmol/m ³)
C _{A0}	initial concentration of A at solid (catalyst) surface (kmol/m ³)
C _{AS}	concentration of A at solid (catalyst) surface (kmol/m ³)
C _B	concentration of B (kmol/m ³)
C _{B0}	initial concentration of B in bulk liquid phase (kmol/m ³)
C _{BS}	concentration of B at solid (catalyst) surface (kmol/m ³)
C _C , C _D	concentration of C and D (kmol/m ³)
C _{CS} –C _{D,S}	concentration of C and D at solid (catalyst) surface (kmol/m ³)
C _S	concentration of vacant sites (kmol/m ³)
C _t	total concentration of the sites (kmol/m ³)
k ₁ , k ₂ , k ₃	surface reaction rate constant for forward reaction
k' ₁ , k' ₂ , k' ₃	Surface reaction rate constant for reverse reaction
K ₁ , K ₂ , K ₃	surface reaction equilibrium constants
K _A	adsorption equilibrium constant for A (m ³ /kmol)
K _B	adsorption equilibrium constant for B (m ³ /kmol)
K _C , K _{D_i}	adsorption equilibrium constants for C and D _i (m ³ /kmol)
k _{SR}	second order rate constant (m ⁶ kmol ⁻¹ kg ⁻¹ s ⁻¹)
k _t	dimensionless constant
r _o	overall rate of reaction based on liquid phase volume (kmol m ⁻³ s ⁻¹)
S	vacant site
t	time (s)
w	catalyst loading (kg/m ³) of liquid phase
X _A	fractional conversion of A
X _B	fractional conversion of B

on the formation of cyclohexylmethoxyphenyl ether and therefore this study was undertaken. A variety of solid acids such as Amberlyst-15, Indion-130 (both cation exchange resins), Filtrol-24 (acid treated montmorillonite clay) and cesium-modified dodecatungstophosphoric acid supported over K-10 montmorillonite clay (20% (w/w) Cs_{2.5}H_{0.5}PW₁₂O₄₀/K-10) and sulphated zirconia were screened to maximize the selectivity to the ether.

2. Experimental

2.1. Chemicals and catalysts

Guaiacol and cyclohexene were obtained from M/s s.d. Fine Chemicals Pvt. Ltd., Mumbai, India. Amberlyst-15 was obtained from Rohm and Haas, USA and Filtrol-24 from Engelhard, USA.

All other chemicals were obtained from M/s s.d. Fine Chemicals Pvt. Ltd., Mumbai, India.

The following catalysts were prepared by well-developed procedures and characterised in our laboratory: twenty percent (w/w) dodecatungstophosphoric acid (DTP/K-10) [22,23], 20% (w/w) Cs_{2.5}H_{0.5}PW₁₂O₄₀/K-10 [24,25], 20% (w/w) ZnCl₂/K-10 montmorillonite clay [26], 20% (w/w) FeCl₃/K-10 montmorillonite clay [27]. Sulphated zirconia [28,29] was prepared by adding aqueous ammonia solution to zirconium oxychloride solution at a pH of 10. The precipitate was thoroughly washed with distilled water and made free from ammonia and chloride ions. It was dried in an oven at 120 °C for 24 h. The sulphation of the zirconia was done using 15 ml g⁻¹ of 0.5 M sulphuric acid. It was dried at 110 °C and calcined at 650 °C for 3 h. All the catalysts were dried in oven at 110 °C for 1 h before use.

2.2. Experimental setup

All experimental studies were conducted in a standard glass reactor of 5 cm i.d. and 10 cm height with four glass baffles and a four bladed disc turbine impeller located at a height of 0.5 cm from the bottom of the vessel and mechanically agitated with an electric motor. The reactor was kept in an isothermal oil bath where the temperature was maintained at the desired level through proper control.

2.3. Experimental methodology

In all the experiments, the guaiacol–catalyst slurry was heated first to the desired reaction temperature with stirring. Cyclohexene was then added to the reactor at the reaction temperature. The moment of addition of cyclohexene into the reactor was taken as the starting time of the reaction. In a typical reaction, 0.226 mol of guaiacol were reacted with 0.045 mol of cyclohexene with 0.03 gm/cm³ catalyst loading of the total volume of the reaction mixture. The total volume of the reaction mixture was 30 ml. The reaction was carried out at 80 °C at a speed agitation of 1000 rpm.

2.4. Analysis

Clear liquid samples were withdrawn periodically and GC analyses were performed on (Chemito Model 8510) by using a stainless steel column (3.25 mm × 4 m) packed with a liquid stationary phase of 10% OV-17. The injector and detector were kept at 300 °C. The oven temperature was programmed from 100 to 300 °C with a ramp rate of 10 °C/min. Nitrogen flow was used as the carrier gas and its flow rate was 0.5 ml/s. The conversions were based on the disappearance of cyclohexene in the reaction mixture. The products were confirmed by the GC–MS and their physical constants.

2.5. Reaction chemistry

The reaction scheme for Friedel–Crafts alkylation of guaiacol with cyclohexene over a solid acid catalyst is shown in Fig. 1. This reaction leads to the formation of mixture of

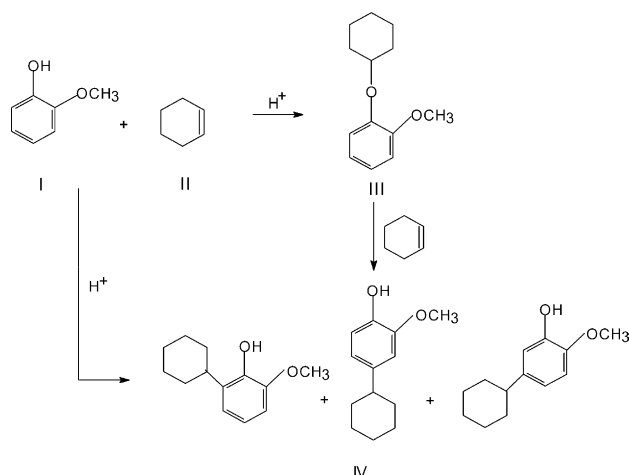


Fig. 1. Reaction scheme for the reaction between guaiacol with cyclohexene in presence of sulphated zirconia.

O-alkylated phenol, namely, cyclohexylmethoxyphenyl ether and three isomers of *C*-alkylated guaiacol (IV), namely, 2-, 3-, and 4-cyclohexyl-2-methoxy phenol which were confirmed by GC–MS. The solid acid catalyst protonates cyclohexene to get a carbocation which then attacks on guaiacol to give the above alkylated products (Figs. 2 and 3).

3. Results and discussion

3.1. Effect of various catalysts

Tables 1 and 2 compare the performance of different catalysts in the conversion of cyclohexene and selectivity of products.

The experiments were carried out under identical set of conditions. A 0.05 g/cm³ loading of catalyst based on the organic volume of the reaction mixture was taken and the temperature was maintained at 80 °C. The mole ratio of guaiacol to cyclohexene was kept at 5:1 with a speed of 1000 rpm. The purpose of using these catalysts was to study the effect of nature of acidity, its strength and pore size distribution and to achieve selective *O*-alkylation. The acid strength of all catalysts was determined by drying the catalysts under vacuum at 120 °C for 6 h by means of temperature-programmed desorption of ammonia. This has been already reported by us earlier [17,30,31] and hence the details

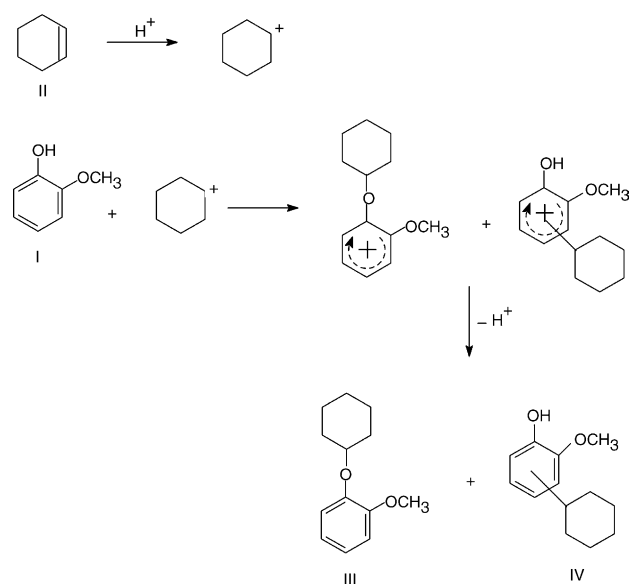


Fig. 2. Mechanism for reaction between guaiacol with cyclohexene.

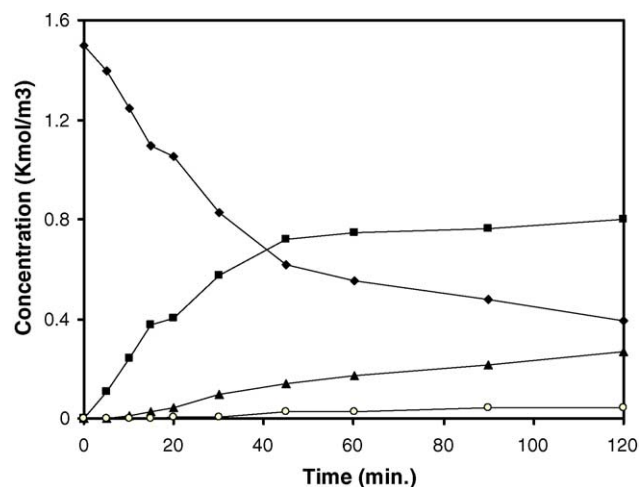


Fig. 3. Concentration profile of various products in alkylation of guaiacol with cyclohexene. Guaiacol 0.226 mol, cyclohexene 0.045 mol, sulphated zirconia 0.03 g/cm³, temperature 80 °C and speed of agitation 1000 rpm; (◆) cyclohexane; (■) *O*-alkylated product; (▲) *C*-alkylated product; (○) dialkylated product.

Table 1
Effect of various catalysts

Catalyst	Conversion of cyclohexene (%)	Selectivity (%)		
		<i>O</i> -alkylated product	<i>C</i> -alkylated products	Dialkylated product
Amberlyst-15	96	1	94	5
Indion-130	77	20	71	9
Filtrol-24	43	61	35	4
20% (w/w) DTP/K-10	61	57	37	6
20% (w/w) Cs-DTP/K-10	81	40	51	9
20% (w/w) ZnCl ₂ /K-10	0	0	0	0
20% (w/w) FeCl ₃ /K10	0	0	0	0
Sulphated zirconia	74	68	27	5

Guaiacol 0.226 mol, cyclohexene 0.045 mol, sulphated zirconia 0.05 g/cm³, temperature 80 °C, speed of agitation 1000 rpm and time 120 min.

Table 2
Physical properties of catalysts

Physical property	Filtrol-24	20% (w/w) DTP/K-10 clay	Sulphated zirconia	Amberlyst-15	20% (w/w) Cesium substituted DTP/K-10 clay	20% (w/w) ZnCl ₂ /K-10 clay	20% (w/w) FeCl ₃ /K-10 clay
Source	Englehard	Prepared	Prepared	Rohm and Hass	Prepared	Prepared	Prepared
Size (µm)	30–400	50–200	50–300	500	50–200	50–200	50–200
Surface area (m ² /g)	350	107	100	55	207	145	145
Average pore diameter (nm)	7.5	7.1	2.8	ND	5.8	6.8	6.8
Porosity (vol.%)	32	25	22	30–35	ND	28	28
Maximum operating temperature (°C)	300	285	650	150	300	285	285
Type of acidity (B or L)	Mainly B	Mainly B	B and L	Mainly B	Mainly B	Only L	Only L
Cation exchange capacity (CEC; mequiv/g)	0.3	0.39	ND	4.9	0.29	ND	ND

ND: no data available; B: Brønsted; L: Lewis.

are avoided. It is evident that Amberlyst-15 and Indion-130, both ion exchange resins, contain only Brønsted acidity and hence they gave selectivity for *C*-alkylated products [32] whereas 20% (w/w) DTP/K-10 and sulphated zirconia contains both Brønsted and Lewis acidity. The conversion of cyclohexene is excellent by using these catalysts and gave good selectivity for the ether. Yadav and co-workers observed the same trend [20,21]. Twenty percent (w/w) ZnCl₂/K-10 and 20% (w/w) FeCl₃/K-10 did not show any activity at these reaction conditions even though they contain only Lewis acidity. It appears that the pore sizes of these catalysts pose considerable intra-particle resistance for the reactant guaiacol to access the catalytic sites. Sulphated zirconia contains a large number of mesopores, is a solid superacid containing more Lewis acids and hence the bulky *O*-product formed easily. Since sulphated zirconia gave good conversion (74%) and maximum selectivity for *O*-alkylated product (72%), all further experiments were carried out by using sulphated zirconia.

3.2. Effect of speed of agitation

The effect of speed of agitation was studied at temperature of 80 °C for a catalyst loading of 0.03 gm/cm³ loading as shown in Fig. 4. It was found that in the range of stirrer speeds 800–1200 rpm, there was no effect of the speed of agitation on the rates of reaction and selectivity of products after 1000 rpm. This showed that in the range of stirrer speeds employed the reaction was free from external mass transfer resistance. Hence, all further experiments were carried out at 1000 rpm. A theoretical analysis of the assessment of external mass transfer of this theory for general slurry reactions are given elsewhere [33]. It was found that there was no effect of external mass transfer limitation.

3.3. 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. The catalyst loading was varied over a range of 0.01–0.05 g/cm³ on the basis of total

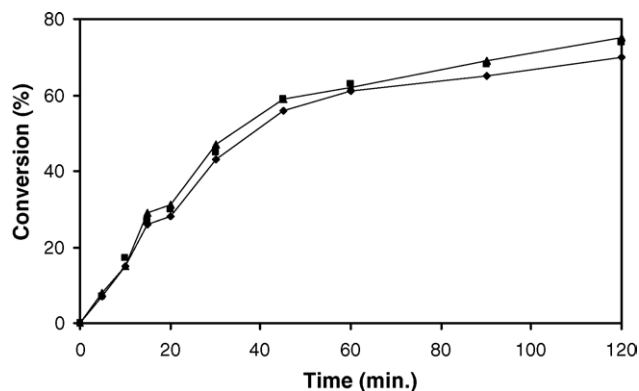


Fig. 4. Effect of speed of agitation. Guaiacol 0.226 mol, cyclohexene 0.045 mol, sulphated zirconia 0.03 g/cm³ and temperature 80 °C; (◆) 800 rpm; (■) 1000 rpm; (▲) 1200 rpm.

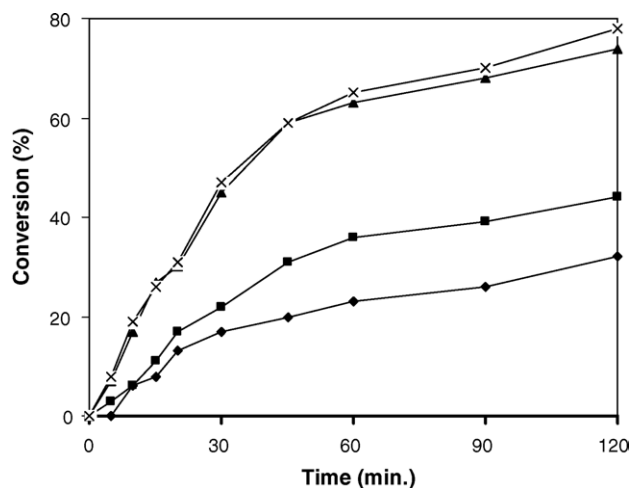


Fig. 5. Effect of catalyst loading. Guaiacol 0.226 mol, cyclohexene 0.045 mol, speed of agitation 1000 rpm and temperature 80 °C; (◆) 0.01 g/cm³; (■) 0.02 g/cm³; (▲) 0.03 g/cm³ × 0.05 g/cm³.

volume of reaction mixture. Fig. 5 shows the effect of catalyst loading on the conversion of cyclohexene. The conversion of cyclohexene increases with increasing catalyst loading of S-ZrO₂, which is obviously due to the proportional increase in the number of active sites. However, beyond a catalyst loading of 0.03 g/cm³, there was no significant increase in the conversion and hence all further experiments were carried out at this catalyst loading.

3.4. Proof of absence of intra-particle resistance

The effect of particle size of the catalyst on the reaction rate was studied by taking three different particle size ranges 75–200 μm to assess the influence of intra particle resistance (Fig. 6). For an average particle size of 90 μm, there was no effect of particle size on the conversion of cyclohexene, which in turn supported the fact that the intra-particle diffusion resistance was

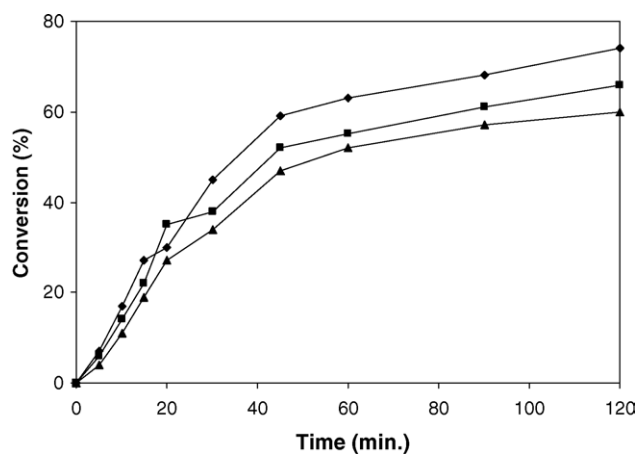


Fig. 6. Effect of particle size. Guaiacol 0.226 mol, cyclohexene 0.045 mol, sulphated zirconia 0.03 g/cm³, speed of agitation 1000 rpm and temperature 80 °C; (◆) 75–90 μm; (■) 125–150 μm; (▲) 160–200 μm.

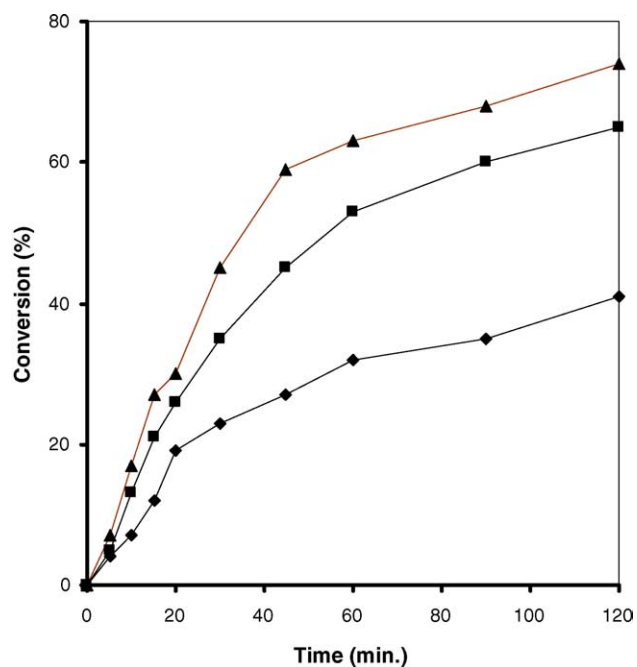


Fig. 7. Effect of mole ratio. Guaiacol:cyclohexene, sulphated zirconia 0.03 g/cm³, speed of agitation 1000 rpm and temperature 80 °C; (◆) 1:1; (■) 3:1; (▲) 5:1.

absent. This was further confirmed by using the Wietz–Prater modulus or criterion [34].

3.5. Effect of mole ratio

The mole ratio of guaiacol to cyclohexene was varied from 1:1 to 5:1 to assess its effect on the rate and selectivity. The overall reaction rate of cyclohexene increased with an increase in the mole ratio of guaiacol to cyclohexene from 1:1 to 5:1. Thus, all the subsequent reactions were carried out with a mole ratio of 5:1. The effect is shown in Fig. 7. This increase in overall rate of alkylation with an increase in mole ratio of guaiacol to cyclohexene can be explained by concept of activity. It appears that with an increase in amount of guaiacol, the activity of cyclohexene increases results in increase in the rate of alkylation reaction. It is also assumed that lower the concentration of cyclohexene, more the adsorption of cyclohexene on the catalyst sites and therefore, more availability of cyclohexenium cation to react with guaiacol. The selectivity for the various products was affected marginally by the change in mole ratio.

3.6. Effect of temperature

The effect of temperature on conversion and selectivity of products was studied in the range of 60–80 °C. With an increase in the temperature from 60 to 80 °C, the rate of reaction increased remarkably but the selectivity for the ether decreased from 89% to 81% for the same conversion level (42% of cyclohexene under identical condition). It appears, therefore, that the alkylation reaction is of higher activation energy than the etherification. No oligomerisation of cyclohexene was noticed in this temperature range. Yadav and Goel [35] have shown earlier that

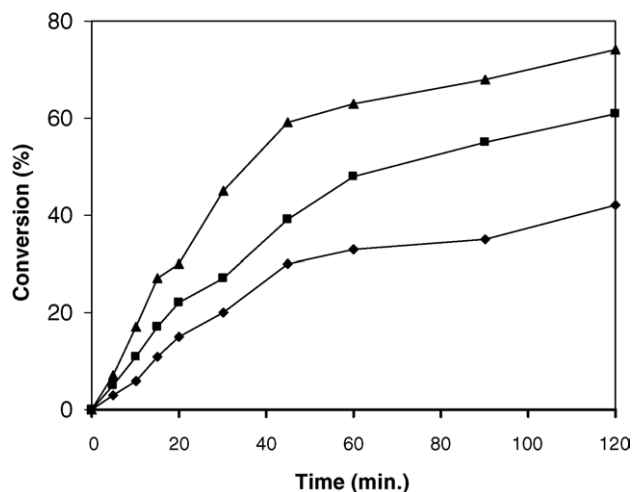


Fig. 8. Effect of temperature. Guaiacol 0.226 mol, cyclohexene 0.045 mol, sulphated zirconia 0.03 g/cm³ and speed of agitation 1000 rpm; (♦) 60 °C; (■) 70 °C; (▲) 80 °C.

oligomerisation of cyclohexene did not occur below 100 °C. The effect of temperature on the overall reaction rate is shown in Fig. 8.

3.7. Reusability of catalyst

After the reaction the catalyst was filtered and then refluxed with 50 cm³ cyclohexane and thereafter with 50 cm³ with methanol for 30 min in order to remove any adsorbed material from catalyst surface and pores and then dried at 120 °C. It was also calcined at 500 °C for 3 h and then cooled to room temperature and weighed. On an average, there was attrition of particles during intense agitation and some loss of catalyst during filtration. This loss varied between 5% and 8% on an average. Two types of experiments were performed to establish the reusability. In one type of experiments, the lost catalyst was made up with fresh catalyst and the activity was tested. In another type, the reactants were reduced proportionately to get the same catalyst loading (0.03 g/cm³ of liquid phase, Table 3). Both types of experiments gave the same initial rates of reactions and final conversions were within 2% of each other. This demonstrated that the catalyst was stable and retained its activity. In subsequent experiments, the same procedure was followed. The catalyst was

Table 3
Reusability of catalyst

Run no.	% Conversion of cyclohexene	
	Type I (make up cat)	Type II (no make up cat)
Fresh	74.0	74.0
First reuse	74.5	73.5
Second reuse	75.5	73.3
Third reuse	74.6	72.0
Fourth reuse	74.1	72.2

Type I—guaiacol 0.226 mol, cyclohexene 0.045 mol and sulphated zirconia 0.03 g/cm³; type II—sulphated zirconia 0.03 g/cm³ of liquid phase. Reactant moles reduced accordingly keeping the same mole ratio. Temperature 80 °C, speed of agitation 1000 rpm and time 120 min.

stable and reusable five times without any loss of activity. There was no change in the selectivity.

Further experiments were done to see if there was any leaching of acid sites in the liquid phase. The stability was tested by stopping the reaction after 1 h and quenching the reaction mixture immediately to arrest the reaction and filtering the catalyst. The clear reaction mass was then recharged to the reactor and heated to 80 °C under agitation, and sampling was done, as in the control experiments. There was practically no conversion during next two hours. This also suggested that the catalyst was stable and reusable.

3.8. Reaction kinetics

From the calculated values of mass transfer rates of A and B and initial observed rate of reaction, it is evident that the rate is independent of the external mass transfer effects. It is also seen from the values of activation energy, that the intra-particle diffusion resistance is absent. Thus, the reaction could be controlled by one of the following steps, namely (a) adsorption (b) surface reaction or (c) desorption. Therefore, for further development of model, the actual mechanism was undertaken. It is assumed that guaiacol and cyclohexene adsorb weakly on catalytic surface. It is the guaiacol (B) from the liquid phase that reacts with chemisorbed AS, accordingly to Eley–Rideal mechanism.

3.8.1. Adsorption

Adsorption of cyclohexene:

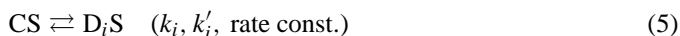
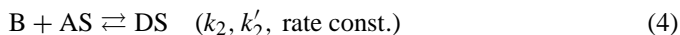
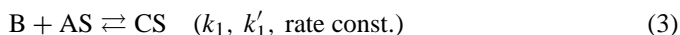


adsorption of guaiacol:



3.8.2. Surface reaction formation of *O*- and *C*-alkylated products (*C* and *D*)

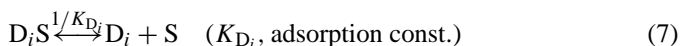
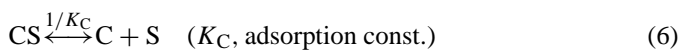
Surface reaction formation of *O*- and *C*-alkylated products (*C* and *D*):



Eq. (5) represents three parallel reactions leading to *D*₁, *D*₂ and *D*₃ isomers.

3.8.3. Desorption

Desorption of three alkylated products from the site can be represented as



The total concentration of the sites, *C*_t expressed in mol/g of catalyst is given by

$$C_t = k_t w = C_S + C_{AS} + C_{BS} + C_{CS} + C_{D_iS} \quad (8)$$

where C_S is the concentration of vacant sites, kmol/m^3 of catalyst.

The various models can now be developed to determine the overall rate of reaction.

3.8.4. Surface reaction controlled model

The surface reaction controlling mechanism is most commonly found to control several reactions and is considered first. If the surface reaction between chemisorbed AS with B from the liquid phase leading to all parallel reactions, is rate controlling, then overall rate of reaction (r_{oi}) of B with AS:

= sum of all net rates of various surface complexes given

by equation

$$= k_1 C_B C_{AS} - k'_1 C_{CS} + k_2 C_B C_{AS} - k'_2 C_{D_i} S + k_4 C_{CS} - k'_4 C_{D_i} S \quad (9)$$

where various equilibrium constants are given by the appropriate equations.

It is essential to substitute the concentrations of surface species, e.g.:

$$C_{AS} = K_A C_A C_S, \quad C_{CS} = K_C C_C C_S \quad (10)$$

etc., where K_A , K_C , etc., are adsorption equilibrium constants.

Putting the appropriate values of concentrations in equation, the following is obtained

$$C_S = \frac{C_t}{1 + K_A C_A + K_B C_B + K_C C_C + K_{D_i} C_{D_i}} \quad (11)$$

Replacing the total concentration of sites by w , the solid loading in g/cm^3 of liquid phase, where $C_t \propto w$ or, $C_t = k_t w$.

Here k_t is a constant.

$$C_S = \frac{k_t w}{1 + K_A C_A + K_B C_B + K_C C_C + K_{D_i} C_{D_i}} \quad (12)$$

Putting Eq. (10) in (9):

$$r_o = [K_A(k_1 + k_3 + k_2)C_B C_A + K_C(k_4 - k'_1)C_C + (K_A k_2 C_A + k_5 K_C C_C) - K_D(k'_2 + k'_4)C_D] \times \left[\frac{k_t w}{1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D} \right] \quad (13)$$

Eq. (13) suggests that the relative values of the rate constants, equilibrium constants and the concentrations of the various species will govern the overall rate of reaction of chemisorbed cyclohexene (AS) with guaiacol (B) from the liquid phase.

Assuming weak adsorption of all species and negligible reversible reactions, Eq. (13) is converted to

$$r_o = k_R K_A C_A C_B w \quad (14)$$

where $k_R = k_t(k_1 + k_2 + k_3)$.

$$-\frac{dC_A}{dt} = K_A k_R C_A C_B w$$

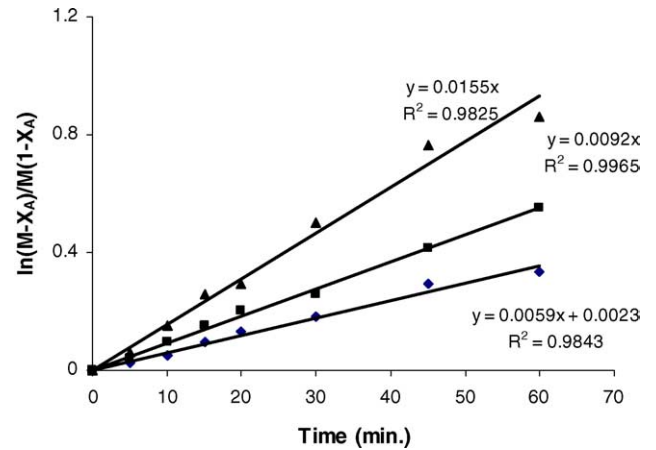


Fig. 9. Typical second-order plot at various temperatures. Guaiacol 0.226 mol, cyclohexene 0.045 mol, sulphated zirconia 0.03 g/cm^3 , temperature 80 °C and speed of agitation 1000 rpm; (◆) 60 °C; (■) 70 °C; (▲) 80 °C.

$$-\frac{dC_A}{dt} = K_A k_R w C_{A0}(1 - X_A)C_{B0}(1 - X_B) = K_A k_R w C_{A0}^2(1 - X_A)(M - X_A) \quad (15)$$

where $M = C_{B0}/C_{A0}$ (M = ratio of initial molar concentration), and $k_{SR} = k_R K_A$

This on integration leads to

$$\ln \frac{M - X_A}{M(1 - X_A)} = \ln \frac{C_B C_{A0}}{C_{B0} C_A} = (C_{B0} - C_{A0})k_{SR} w t \quad (16)$$

Further, $M = C_{B0}/C_{A0}$.

Hence, Eq. (10) reduces to

$$\ln \frac{M - X_A}{M(1 - X_A)} = k_{SR} C_{A0} w (M - 1) t \quad (17)$$

Hence, a plot of $\ln((M - X_A)/M(1 - X_A))$ versus t would be a straight line with slope equal to $C_{A0} k_{SR} w (M - 1)$ from which the rate constant k_{SR} could be evaluated. Moreover, the linearity of this plot would confirm the second order behavior of the reaction. Fig. 9 shows the validity of this theory at different temperatures.

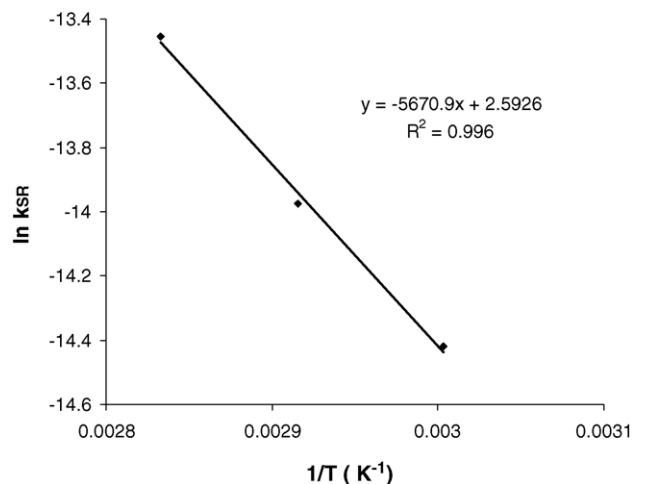


Fig. 10. Arrhenius plot of $\ln k_{SR}$ vs. $1/T$.

From the slopes of lines in Fig. 9, the rate constants (k_{SR}) at different temperature were calculated as

$$k_{SR}(60\text{ }^{\circ}\text{C}) = 5.46 \times 10^{-7} \text{ m}^6 \text{ kmol kg}^{-1} \text{ s}^{-1},$$

$$k_{SR}(70\text{ }^{\circ}\text{C}) = 8.51 \times 10^{-7} \text{ m}^6 \text{ kmol kg}^{-1} \text{ s}^{-1},$$

$$k_{SR}(80\text{ }^{\circ}\text{C}) = 1.43 \times 10^{-6} \text{ m}^6 \text{ kmol kg}^{-1} \text{ s}^{-1}$$

The Arrhenius plot (Fig. 10) gives the apparent activation energy as 11.03 kcal/mol, which also indicates that the reaction is intrinsically kinetically controlled.

4. Conclusion

Alkylation of guaiacol with cyclohexene over solid acid catalysts leads to the formation of both *O*- and *C*-alkylated products, depending on temperature and nature of catalyst. All these products are useful in a variety of industries. Thus, selective formation of one of the products is quite a challenging task, which would avoid the separation problems and consequently reduce the process costs. Different catalysts having wider acidity and nature of acidity, and pore size distribution were used in this study, such as sulphated zirconia, Amberlyst-15, Filtrol-24, Indion-130, 20% (w/w) dodecatungstophosphoric acid supported on K-10 clay (DTP/K-10) and 20% (w/w) cesium-modified dodecatungstophosphoric acid supported over K-10 clay ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$). Sulphated zirconia was the best catalyst to achieve maximum selectivity for the *O*-alkylated product, cyclohexylmethoxyphenyl ether, which is a valuable perfume and precursor to a number of fine chemicals. The overall reaction rate increased with increase in catalyst loading, reaction temperature and guaiacol:cyclohexene ratio. For selective *O*-alkylation the reaction should be carried out at 80 °C in presence of sulphated zirconia with mole ratio 5:1. The conversion is 74% with 68% selectivity for the ether. The reaction was carried out without using any solvent. Sulphated zirconia is robust and reusable. A kinetic model was developed for this reaction. The activation energy was found to be 11.03 kcal/mol.

Acknowledgements

GDY acknowledges support from the Darbari Seth Professor endowment. GSP is thankful to CSIR, New Delhi for awarding Junior Research Fellowship during this work.

References

- [1] G.D. Yadav, M.S.M. Mujeebur Rahuman, Appl. Catal. A: Gen. 253 (2003) 113.
- [2] G.D. Yadav, N.S. Doshi, Appl. Catal. A: Gen. 236 (2002) 129.
- [3] G.D. Yadav, A.A. Pujari, A.V. Joshi, Green Chem. 1 (1999) 269.
- [4] G.D. Yadav, S.S. Salgaokar, Ind. Eng. Chem. Res. 44 (2005) 1706.
- [5] G.D. Yadav, A.D. Murkute, J. Catal. 224 (2004) 218.
- [6] G.D. Yadav, A.D. Murkute, Langmuir 20 (2004) 11607.
- [7] Z.E. Aliev, S.M. Agaeva, S.B. Bilalor, Prasadki. Smaz. Maslam. 2 (1969) 118 (Russian).
- [8] S.P. Starkav, B.A. Baranor, M.N. Volkotrub, Zr. Priki. Khim. 41 (3) (1969) 688.
- [9] R.R. Read, US Patent 2 178 608 (1941) to Sharp and Dohme Inc.
- [10] R.R. Read, US Patent 2 391 798 (1945) to Sharp and Dohme Inc.
- [11] F. Hoffmann, German 615,448 (1935) to La Roche & Co. A-G.
- [12] Clearfield, G.P.D. Serrete, A.H. Khazi-Syed, Catal. Today 20 (1994) 295.
- [13] W. Hertl, Langmuir 5 (1989) 96.
- [14] V. Adeeva, J.W. de Haan, J. Janchen, G.D. Lei, V. Schunemann, L.J.M. van de Ven, W.M.H. Sachtler, R.A. van Santen, J. Catal. 151 (1995) 364.
- [15] F. Pinna, N. Signoretto, G. Strukul, G. Cerrato, C. Morterra, Catal. Lett. 26 (1994) 339.
- [16] P.S. Kumbhar, V.M. Yadav, G.D. Yadav, in: D.E. Layden (Ed.), Chemically Modified Oxide Surfaces, Gordon and Breach, New York, 1989.
- [17] G.D. Yadav, J.J. Nair, Micropor. Mesopor. Mater. 33 (1999) 1.
- [18] A. Hino, K. Arata, J. Chem. Soc., Chem. Commun. 24 (1980) 1148.
- [19] X. Song, A. Sayari, Catal. Rev. Sci. Eng. 38 (3) (1996) 329.
- [20] G.D. Yadav, P. Ramesh, Can. J. Chem. Eng. 78 (2000) 323.
- [21] G.D. Yadav, P. Kumar, Appl. Catal. A: Gen. 28 (6) (2005) 61–70.
- [22] G.D. Yadav, N. Kirthivasan, Appl. Catal. A: Gen. 154 (1997) 23.
- [23] G.D. Yadav, N.S. Asthana, Ind. Eng. Chem. Res. 41 (2002) 5565.
- [24] G.D. Yadav, N.S. Asthana, S.S. Salgaonkar, Clean Tech. Environ. Policy 6 (2004) 105.
- [25] G.D. Yadav, N.S. Asthana, V.S. Kamble, J. Catal. 217 (1) (2003) 88.
- [26] G.D. Yadav, N. Kirthivasan, J. Chem. Soc., Chem. Commun. (1995) 203.
- [27] G.D. Yadav, N.S. Doshi, Org. Proc. Res. Dev. 6 (2002) 263–272.
- [28] P.S. Kumbhar, V.M. Yadav, G.D. Yadav, in: D.E. Layden (Ed.), Chemically Modified Oxide Surfaces, Gordon and Breach, New York, 1989.
- [29] G.D. Yadav, A.A. Pujari, Green Chem. 1 (2) (1999) 69.
- [30] G.D. Yadav, N. Kirthivasan, in: Jonathan P. Blitz, Charles B. Little (Eds.), Fundamental and Applied Aspects of Chemically Modified Surfaces, Royal Society of Chemistry, UK, 1999, p. 254.
- [31] P.S. Kumbhar, G.D. Yadav, Chem. Eng. Sci. 44 (1989) 2535.
- [32] A. Chakrabati, M.M. Sharma, React. Polym. 17 (1992) 331.
- [33] G.D. Yadav, S. Sengupta, Org. Proc. Res. Dev. 6 (2002) 256.
- [34] H.S. Fogler, Elements of Chemical Reaction Engineering, Prentice-Hall, New Delhi, 1995.
- [35] G.D. Yadav, P.K. Goel, Green Chem. 2 (2) (2000) 71.