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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

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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 ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$/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.

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 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 actives 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

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* 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).

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Nomenclature

A	reactant species A, cyclohexene
B	reactant species B, guaiacol
AS, BS, CS, D_iS	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_iS}	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) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/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 Filtol-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) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 [24,25], 20% (w/w) $ZnCl_2$/K-10 montmorillonite clay [26], 20% (w/w) $FeCl_3$/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/cm^3 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