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Alkylation of phenol with cyclohexene over solid acids: Insight in selectivity of O- versus C-alkylation

Ganapati D. Yadav *, Parveen Kumar

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

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Abstract

Alkylation of phenol with cyclohexene with acid catalysts leads to the formation of both O- and C-alkylated products, which are all useful in a variety of industries. The O-alkylated product cyclohexyl phenyl ether is a valuable perfume and can also serve as a precursor to diphenyl ether, a very important bulk chemical. The efficacy of various acid catalysts such as sulphated zirconia, sulphonic acid treated hexagonal mesoporous silica (SO_3-HMS), 20% (w/w) dodecatungstophospheric acid (DTP) supported on K-10 clay, 20% (w/w) cesium salt of DTP ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) supported on K-10 clay (Cs-DTP/K-10) and 20% (w/w) DTP/HMS was studied to improve the selectivity to cyclohexyl phenyl ether. A mixture of 2-cyclohexylphenol, 4-cyclohexylphenol and cyclohexyl phenyl ether was obtained with different selectivities. However, 20% (w/w) DTP/K-10 clay was the most active and selective catalyst for O-alkylation in the range of 45–70 °C at atmospheric pressure. The selectivity to O- versus C-alkylation is strongly dependent on temperature, and at lower temperatures, the selectivity to cyclohexyl phenyl ether increases. The best operating temperature is 60 °C. A mathematical model is built to interpret the kinetic data and develop a mechanism.

Keywords: Alkylation; Selectivity; Phenol; Cyclohexene; Cyclohexyl phenyl ether; 2-Cyclohexyl phenol; 4-Cyclohexyl phenol; Heteropoly acid; Clay; Dodectatungstophosphoric acid; Sulphated zirconia; Hexagonal mesoporous silica

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1. Introduction

Solid acid catalysts are widely used for the development of green technology to replace the traditional polluting catalysts in organic process industries employing alkylation, acylation, isomerization, nitration, condensation, cracking, and esterification, etc. [1]. Zeolites, acid treated clays, ion exchange resins and supported heteropoly acids are investigated by several groups for their applications in pharmaceutical, perfumery, agro-chemicals, dye-stuffs, intermediates and specialty chemical industries. Our laboratory has been engaged in novel applications and modelling of catalysis by sulphated zirconia [2–7], UDCaT series[8–20], clay supported heteropoly acids [21–27], Cs-HPA/K-10 [28–31], HMS supported HPA [32], ion exchange resins [33–42] and zeolites [43,44] for a variety of bulk and fine chemical processes involving alkylation, acylation, esterification, nitration, isomerization, etherification, cracking, oligomerisation, cyclization, hydration, and dehydration, etc. The acronym UDCaT stands for the series of catalysts developed in our laboratory (named after University Institute of Chemical Technology).

Alkylation of phenol with cyclohexene has attracted attention of many researchers because of its industrial and academic relevance. Alkylation of phenol with cyclohexene leads to a variety of products such as 4-cyclohexylphenol, 2-cyclohexylphenol, and cyclohexyl phenyl ether depending on catalyst and reaction conditions. Cyclohexyl phenyl ether serves as a perfumery compound and its dehydrogenation leads to diphenyl oxide (DPO), which is very relevant. DPO

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* Corresponding author. Tel.: +91 22 24102121; fax: +91 22 24145614.
E-mail addresses: gdyadav@yahoo.com, gdyadav@udct.org
(G.D. Yadav).

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is made from a polluting route or energy intensive radioactive thoria catalysed dehydration of phenol or from chlorobenzene leading to effluent problems. 4-Cyclohexylphenol and 2-cyclohexylphenol can be used precursors of *o*- and *p*-phenylphenol [45], which are again precursors to a number of industrially valuable products.

Nomenclature

a_P	solid–liquid interfacial area, cm^2/cm^3 of liquid phase
A	reactant species A, cyclohexene
B	reactant species B, phenol
BS	chemisorbed B
C	cyclohexyl phenyl ether
C_A	concentration of A (g mol/cm^3)
C_{AO}	initial concentration of A at solid (catalyst) surface (mol/cm^3)
C_{AS}	concentration of A at solid (catalyst) surface, (mol/cm^3)
C_B	concentration of B (mol/cm^3)
C_{BO}	initial concentration of B in bulk liquid phase, mol/cm^3
C_{BS}	concentration of B at solid (catalyst) surface, mol/cm^3
C_C, C_D	concentration of C and D, mol/cm^3
C_{CS}, C_{DS}	concentration of C and D at solid (catalyst) surface, mol/cm^3
C_S	concentration of vacant sites, mol/cm^3
C_t	total concentration of the sites, mol/cm^3
d_P	diameter of catalyst particle, cm
D	4-cyclohexyl phenol
D_{AB}	diffusion coefficient of A in B, cm^2/s
D_{BA}	diffusion coefficient of B in A, cm^2/s
E	4-cyclohexyl phenol
k_1	surface reaction rate constant for forward reaction
k_1'	surface reaction rate constant for reverse reaction
k_{SR}	second order rate constant, cm^6 g mol^{-1} g^{-1} s^{-1}
k_t	dimensionless constant
K_1	surface reaction equilibrium constant, k_1/k_1'
$K_{A\ldots}$	K_E adsorption equilibrium constant for A, B, C, D, and E cm^3/mol
r_o	overall rate of reaction based on liquid phase volume, g mol cm^{-3} s^{-1}
r_{oi}	initial rate of reaction, g mol cm^{-3} s^{-1}
R_B	rate of reaction of B, g mol cm^{-3} s^{-1}
S	vacant site
Sh	sherwood number
w	catalyst loading, g/cm^3 of liquid phase
X_A	fractional conversion of A
ρ_P	density of catalyst particle, g/cm^3

Alkylation of phenol with cyclohexene and cyclohexanol is reported over HY and modified HY zeolites at 140–225 °C [46]. However, a limited information is available on the O-alkylation. The catalysts used for the synthesis of cyclohexylphenyl ether are ion exchange resins, Amberlyst 15, AmberliteIR-120, Nafion NR-50, and Filtrol-24 [45].

Heteropoly acids are very important class of acid and redox catalysts. The novelty of clay supported heteropolyacids as reusable benign catalysts was reported by us [21] for the first time and a series of commercially important reactions were studied [21–27]. We have also developed a novel nano-catalyst using partially substituted dodecatungstophosphoric (DTP) acid with cesium and supporting it on acid activated clay. Thus, nanoparticles of 20% (w/w) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$b were created in the pore network of acid treated K-10 clay (designated as Cs-DTP/K-10 in subsequent discussions) and used for a number of acid catalyzed reactions [28–31].

The current work was undertaken to asses the suitability of various solid acid catalysts such as sulphated zirconia, sulphonic acid treated silica, 20% (w/w) dodecatungstophospheric acid supported on K-10 clay, 20% (w/w) Cs-DTP/K-10 clay and 20% (w/w) DTP/HMS for predominantly producing cyclohexyl phenyl ether, including the development of kinetics and mechanism.

2. Experimental

2.1. Chemicals

Cyclohexene and dodecatungstophosphoric (DTP) acid were procured commercially from M/s. s.d. fine Chemicals Pvt. Ltd,. Mumbai, India. Phenol was obtained from Merck Fine Chemicals, Mumbai, India and K-10 clay from Fluka, Germany.

Sulphated zirconia [1] and 20% (w/w) DTP/K-10 clay [2] were prepared by established procedures in our laboratory. K-10 clay was first impregnated with aqueous solution of Cs^+ precursor (Cesium chloride), dried at 110 °C and calcined at 300 °C. DTP was then impregnated on the support, from a methanolic solution, dried at 110 °C for 12 h and calcined at 300 °C for 3 h. Thus, 20% (w/w) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 was dried at 110 °C for 12 h and the calcined at 300 °C for 3 h. Bulk $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was prepared by adding the Cs precursor solution dropwise to the DTP solution while stirring. The resulting precipitate was dried at 110 °C for 12 h and calcined at 300 °C for 3 h. All catalysts were powdered and dried at 120 °C for 3 h prior to their use. For the synthesis of sulphated zirconia, a known amount of zirconium oxychloride was dissolved in deionized water and precipitated using aqueous ammonia. The precipitate obtained was washed and dried. The dry cake was crushed to desired particle size and sulphated with 1 N H_2SO_4. It was calcined in air at 650 °C for 3 h to give sulphated zirconia [2–5].