

Solid-acid-catalyzed alkylation of phenol in aqueous and hydrocarbon solvents

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Introduction

Biomass-derived phenolic oils, obtained from pyrolysis or hydrolysis of lignin, are becoming a promising feedstock to replace fossil resources for the production of fuels and chemicals via catalytic upgrading. In particular, acid-catalyzed C–C bond formation produces alkylated phenolics in the desirable carbon-number range of fuels from reactions of phenolic compounds with small alcohols (from hydrogenation of small carboxylic acids and ketones)[1] or with hydrogenated/hydrodeoxygenated intermediates of phenolics (cycloalcohols or cycloalkenes)[2,3]. When phenol alkylation is performed on solid surfaces in the liquid phase, the catalytic activity, the kinetic mechanism (Langmuir-Hinshelwood, or Eley-Rideal) and the preferred reaction pathway (e.g., C- vs. O-alkylation) depend on the type and strength of acid sites, the size of the nano-environment, the alkylating agent (electrophile), the reaction temperature, as well as the solvent. Herein, we report a detailed kinetic and mechanistic study of phenol alkylation with cyclohexanol/cyclohexene, catalyzed by a range of solid acids containing varying proportions of Brønsted and Lewis sites, in aqueous and non-polar solvents.

Materials and Methods

All chemicals (>98% purity) were obtained from Sigma Aldrich and used without further purification. Commercial MFI (Si/Al = 45, Clariant), BEA (Si/Al = 19 and 75, Clariant and Zeolyst) and FAU (Si/Al = 15 and 40, Zeolyst) zeolites in H-forms and other solid acids (e.g., SAC-13, γ -Al₂O₃) were either used as received or thermally activated before reaction. Alkylation of phenol was performed in a 300 ml Parr autoclave reactor at 393–433 K while stirring at 700 rpm. Aliquots of liquid samples collected after reaction and work-up (extraction or centrifugation) were analyzed on Shimadzu2010 GC and GCMS (QP2010S).

Results and Discussion

Large-pore zeolites (FAU, BEA) were most active for phenol alkylation with cyclohexanol in decalin. Lewis acid sites (LAS) on γ -Al₂O₃ surface were much less active than Brønsted acid sites (BAS) for the alkylation of phenol and afforded the highest ratio of ortho:para substitution products. For phenol-cyclohexanol reactions, alkylation of phenol did not appreciably occur until cyclohexanol was significantly converted on HBEA zeolite (Figure 1). ¹³C distribution in cyclohexene and cyclohexylphenols (reactants: 1-¹³C-phenol and 1-¹³C-cyclohexanol) monitored in situ by NMR provides important mechanistic insights. For both o- and p- monoalkylation, the concentrations of 2-¹³C-cyclohexyl phenols were significantly higher than 1-¹³C-cyclohexyl phenols. If phenol reacted with the carbenium ion directly generated from dehydration of 1-¹³C-cyclohexanol, before significant hydride shift had occurred, most of the C-alkylation products should have contained 1-¹³C-cyclohexyl. Thus,

carbocationic electrophiles directly produced from cyclohexanol dehydration are not able to account for the observed preference for 2-¹³C-cyclohexyl phenols. Instead, these results are consistent with re-adsorption and protonation of cyclohexene at the BAS that forms more 2-¹³C-cyclohexyl carbenium ion than 1-¹³C-cyclohexyl carbenium ion at all reaction times. Alkylation via intramolecular rearrangement of cyclohexyl phenyl ether was also excluded based on the in situ NMR data. Both kinetic and NMR data are in favor of an Eley-Rideal type mechanism.

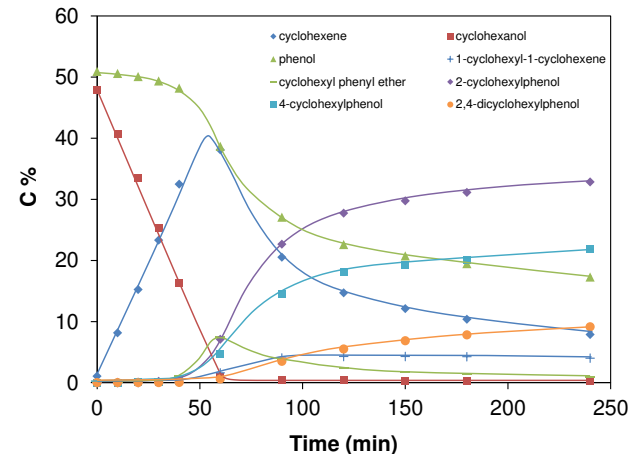


Figure 1. Alkylation of phenol with cyclohexanol as a function of reaction time on HBEA-150 in decalin. Reaction conditions: 5.0 g phenol, 5.0 g cyclohexanol, 0.20 g HBEA-150, 100 mL decalin, stirred at 700 rpm, 160 °C. Only major products are shown in this plot.

Significance

We provide fundamental understanding of why hydronium ion catalyzed alkylation and dehydration is significantly less efficient than the same reactions occurring in non-polar solvents.

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