Liquid-phase alkylation of lignin-derived phenolics on solid acids: towards improved mechanistic understanding and process design

Hui Shi,[a,]* **Yuanshuai Liu,**[a] **Meng Wang,**[b] **Jianzhi Hu,**[b] **Donald M. Camaioni,**[b] **Johannes A. Lercher**[a,b,]*

[a]*Department of Chemistry and Catalysis Research Center, TU München, Lichtenbergstrasse 4, 85748 Garching, Germany;* [b]*Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, 99352, USA*

**Corresponding author, email: hui.shi@mytum.de or johannes.lercher@tum.de*

Abstract: Alkylation of phenolics is of great importance in synthetic chemistry as well as the valorization of lignocellulosic-biomass-derived feedstocks. Using a detailed kinetic and mechanistic study of phenol alkylation with cyclohexanol/cyclohexene, it is shown that alkylation requires the generation of carbenium ions by protonation of intermediately formed alkene. In situ measurements of the reacting species by NMR spectroscopy helped to identify the reaction steps.

Keywords: Alkylation, Biomass, Zeolites, Acid catalysis, Phenolics.

1. Introduction

Biomass-derived phenolic oils, obtained from pyrolysis or hydrolysis of lignin, represent a promising type of feedstock to partly 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 (cycloalkanols or cycloalkenes)[2,3]. This lecture aims to highlight our recent efforts at deciphering several previously unresolved mechanistic details of this old class of reaction in zeolite confines.

2. Experimental

Commercial BEA (Si/Al = 19 and 75), MFI (Si/Al = 45), FAU (Si/Al = 15 and 40) zeolites in protonic forms and other solid acids (e.g., WO_x/ZrO_2, γ-Al_2O_3, Al-MCM-41) were either used as received or thermally activated before reaction. All chemicals (>98% purity, or 99% ^{13}C-enriched 1-^{13}C-labeled phenol and cyclohexanol in NMR experiments) were purchased from Sigma Aldrich and used without further purification. Alkylation reactions of phenol and substituted phenols were carried out in a 300 ml Parr autoclave reactor typically at 393−433 K while stirring at 700 rpm. Aliquots of liquid samples collected during reaction were analyzed on Shimazu2010 GC and GCMS (QP2010S). In situ NMR experiments were carried out on a Varian 500 MHz NMR spectrometer using a 7.5 mm HX MAS probe with a spinning rate of 3.1 kHz at a resonance frequency of 125.7 MHz.[4]

3. Results and discussion

Among the studied solid acids, large-pore zeolites (FAU, BEA) were the most active for phenol alkylation with cyclohexanol in decalin, an apolar solvent with high solubilities of cyclic and aromatic compounds. Lewis acid sites (LAS) on γ-Al_2O_3 surface were much less active than Brønsted acid sites (BAS) for the alkylation of phenol and afforded a much higher ratio (~110) of ortho:para substitution products than those (1–3) on BAS. Interestingly, for phenol-cyclohexanol reactions on zeolites, alkylation of phenol initially occurred at low rates until cyclohexanol was largely (i.e., >70%) dehydrated (Figure 1, left panel). With alcohol as the starting alkylating reagent, there are multiple routes that potentially can generate the electrophile: (1) alkoxonium ion from protonation of alcohol; (2) carbenium ion from alcohol-derived intermediates; (3) carbenium ion from olefin re-adsorption and protonation. In this respect, ^{13}C distribution in cyclohexene and cyclohexylphenol products (reactants: 1-^{13}C-phenol and 1-^{13}C-cyclohexanol) monitored in situ by NMR has provided important insights into the prevalent mechanism.[4] For both ortho- and para-monoalkylation, the concentrations of 2-^{13}C-cyclohexyl phenols were significantly higher than 1-^{13}C-cyclohexyl phenols (Figure 1, right panel). If phenol reacted with the alkoxonium ion or carbenium ion directly generated from dehydration of 1-^{13}C-cyclohexanol before significant hydride shift had occurred, most of the C-alkylation products should have contained 1-^{13}C-cyclohexyl. Thus, electrophiles directly produced from cyclohexanol are not able to account for the observed excess of 2-^{13}C-cyclohexyl phenols. Instead, these results are consistent with re-adsorption and protonation of 1- and 3-^{13}C-cyclohexenes at the BAS that forms more 2-^{13}C-cyclohexyl carbocations than 1-^{13}C-cyclohexyl carbenium ions at all reaction times. Other valuable mechanistic information extracted from the ^{13}C isotope scrambling data (such as cyclohexene isotopomers) will be also discussed.

Cyclohexene is a much more efficient alkylating reagent, inducing rapid alkylation from the beginning of reaction.[4] With cyclohexanol initially added together with cyclohexene, however, all alkylation reactions were drastically retarded and became faster only after a major fraction of cyclohexanol was dehydrated. These observations, taken together with other evidence (to be discussed in this talk), illustrate the fact that BAS is much more significantly occupied by cyclohexanol than by cyclohexene and phenol. The rate acceleration of phenol alkylation (with cyclohexanol) at $t > 400$ min (Figure 1) is, therefore, attributed to the increased activity of carbenium ions produced from olefin re-adsorption and protonation at the BAS, once the alcohol-derived species are significantly depleted by dehydration.

Design criteria for the alkylation processes and experimental results using simulated feeds containing mixed phenolics and alcohols will be presented. We suggest that when alcohol is used as the alkylating reagent, its concentration should be maintained at a low level so that electrophile can be more facilely generated from either dehydration via the monomer species or olefin re-adsorption and protonation (with the latter pathway making more contribution in batch reactor operation), which was indeed experimentally confirmed.

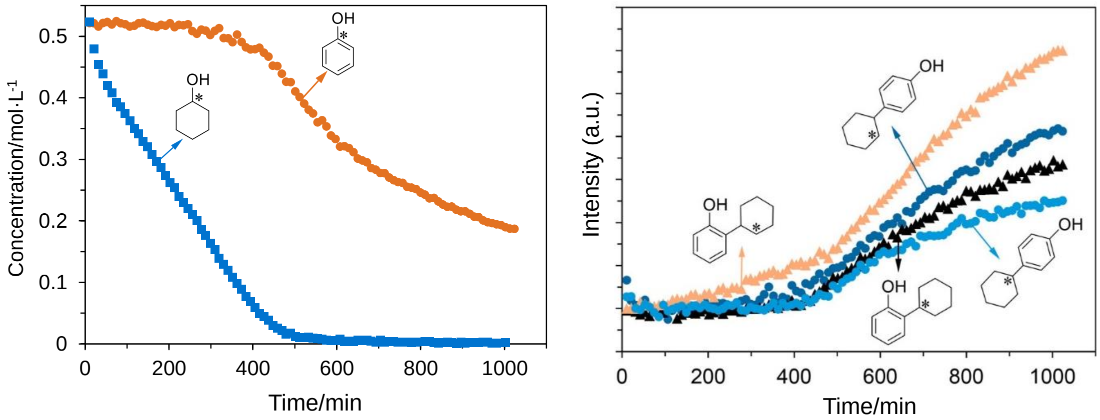

Figure 1. Concentration−time profiles of the two 1-^{13}C-labeled reactants (left panel) and integrated ^{13}C signal intensities of ortho- and para-monoalkylation products (right panel) during phenol alkylation with 1-^{13}C-cyclohexanol on H-BEA (Si/Al = 75) in decalin (unlabeled) as a function of reaction time at 127 ℃. Adapted from ref. [4].

4. Conclusion

Regardless of the alkylating reagent (alcohol or olefin), the effective electrophile for phenol alkylation in large-pore zeolites is always carbenium ion, which is much more facilely generated from olefin adsorption and protonation than from alcohol dehydration.

References

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