The Effects of Solvent on the Furfuryl Alcohol Polymerization Reaction: Characterizations of Molecular Structure and Thermodynamic Properties

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Introduction and Objectives

With declining resources and increasing demands for petroleum, there has been a great interest in (1) the production of energy from biomass and (2) the effective utilization of furanose materials, which arising from the acid-catalyzed dehydration of pentose and hexose. Furfuryl alcohol (FA) has been considered as an important furan commodity and is industrially produced via hydrogenation reaction from furfural derived from selective dehydration of xylose. FA can be converted to levulinic acid (LA) via dehydration and polymerized under acidic conditions.[1,2] The polymerized FA is synthesized by the cationic condensation of FA by acid catalysis. To minimize polyfurfuryl alcohol (PFA) and maximize LA product, fundamental understanding of undesired side reaction, such as coke formation, is required. We have been used a combined Raman spectroscopic and density functional study to understand carbonaceous material known as humin development mechanism.[3] The present study focuses on the identification of the intermediate species structure, mechanism, and rate of PFA during the FA polymerization reaction with different FA/solvents (ethanol, butanol, and iso-butanol) molar ratios.

Results and Discussion

As shown in the figure 1, solvents concentrations or FA/solvents molar ratio, and the kinds of solvents were changed for the FA polymerization reaction. Without solvents, the symmetric C=C (1504 and 1597 cm^{-1}) and C-C (1384 cm^{-1}) ring stretching band intensities in FA spectrum decreased quickly with time and new band was observed to grow at 1654 cm^{-1}. By using density functional theory calculations, we have constructed the Raman spectra to analyze the formation of conjugated diene and diketone molecular species. On the basis of the theoretically calculated diene and diketone spectra, we conclude that

the strong band measured at 1654 cm^{-1} should be assigned to the acyclic C=C bond. Solvents included samples Raman spectra provided that the intensity of 1654 cm^{-1} band is continuously decreased with increasing solvent concentrations at the similar reaction time. This result indicate that different 1504 cm^{-1} and 1654 cm^{-1} peak intensity patterns reflect the important effect of the solvent on the reactivity of FA polymerization reaction.

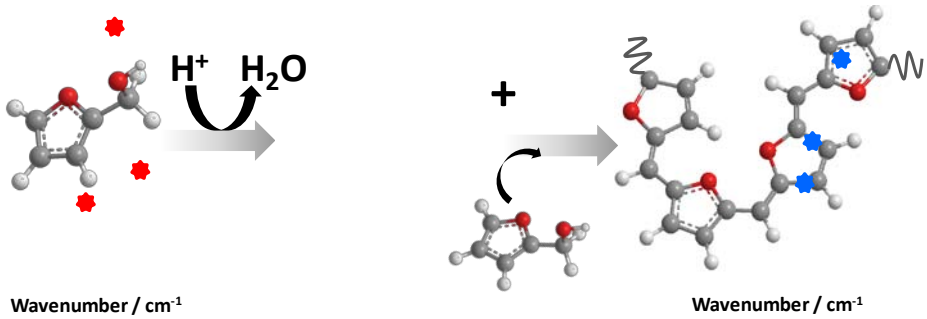

Figure 1. Raman spectra (325 nm) of the FA and PFA. Sample: FA (3 g) and diluted sulfuric acid (SA,1M, 0.04 g) solutions at room temperature in month.

Conclusions

The Raman spectra of various intermediates involved in the acid-catalyzed polymerization of furfuryl alcohol (FA) were calculated by using the B3LYP level of theory and the results were compared with the measured spectra. Based on the measured and calculated Raman spectra, and thermodynamic calculation, the formation of a diene structure from FA monomer is preferred over the formation of a diketone structure. The rate of FA polymerization was decreased with increasing solvent concentrations and was controlled by the FA/solvents molar ratio.

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References

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