ATR-IR Study on the Kinetics of Aqueous Phase Conversion of Biomass over Supported Metal Catalysts

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Introduction and Objectives

Due to the growing interest in the development of renewable, carbon neutral chemicals and transportation fuels, there is growing body of research that aims to adapt existing heterogeneous catalysis processes for biomass conversion. Aqueous phase catalytic processes for biomass conversion are promising,[1] but little is currently known about the reaction pathways of such catalytic systems. The objective of this study is to understand differences in the kinetics and observed surface intermediates formed when flowing aqueous solutions of glycerol and glucose over γ-Al_2O_3 supported metal catalysts by in-situ attenuated total reflectance infra-red (ATR-IR) spectroscopy. The different molecular structure of these reactants is expected to result in different kinetics for aqueous phase reforming and the formation of carbonaceous deposits. Pt/γ-Al_2O_3 was chosen because it is an active catalyst for the aqueous phase reforming of biomass,[2] it is stable during the length of these experiments in the conditions used in this study,[3] and it also has favorable spectroscopic properties.

Results and Discussion

Operando ATR-IR experiments were performed by depositing a layer of Pt/γ-Al_2O_3 directly on the internal reflection element and flowing biomass solution over the catalyst. A 300 mM glycerol solution flow resulted in the formation of dissociated hydrogen, linear, and bridging CO species on the Pt particles, Figure 1 a) 1). The development of these modes occurred significantly after the stabilization of bulk glycerol solution signals at 2 min, indicating kinetic control. Returning to degassed flow resulted in the removal of bulk glycerol from the catalyst pores. Introduction of O_2 saturated water resulted in the rapid oxidative removal of all H and CO species, and a small blue-shift of the 1620 carbonyl as well as the growth of the carbonyl species at 1698 cm^{-1}, shown in Figure 1 a) 3). Under these conditions, carbonyls formed from dehydrogenation chemistry are more strongly bound to the Pt than CO. Irreversibly bound carbonyls will poison the Pt and are likely precursors to humin formation.

Conversion of a 300 mM aqueous glucose solution also resulted in the formation of dissociated hydrogen, linear, and bridging CO on the Pt surface, Figure 1 a) 2), all of

which are less intense and red shifted when compared to glycerol. A study that used dissolved CO and a Pt/γ-Al_2O_3 catalyst suggests the intensity and red shift trends observed here indicate a lower surface concentration.[4] Also, the observed carbonyl modes are more intense than in the case of glycerol, suggesting a higher concentration of carbonaceous deposits on the surface. Even after exposure to dissolved oxygen, Figure 1 a) 4), the carbonyl peaks remain intense. CO formation kinetics were slower in the case of glucose relative to glycerol, as the time to reach a constant linear CO peak took greater than 30 min, compared to 20 min in the case of glycerol, Figure 1 b). The slower initial rate of CO formation from glucose is likely due to its longer carbon chain length, as carbonyl formation was not seen in the first 5 min.

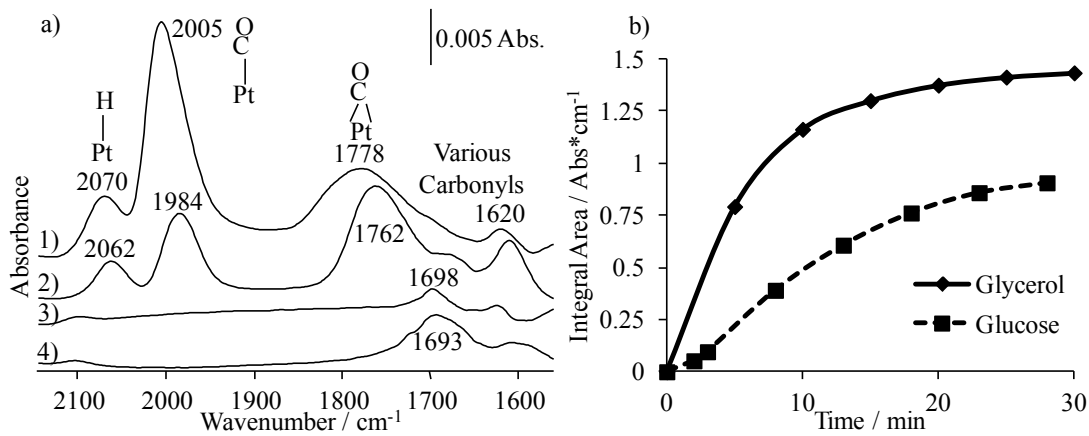

Figure 1. a) ATR-IR Spectra of catalyst layer during water flow post 30 min glycerol exposure in 1), post 30 min glucose exposure in 2), during dissolved oxygen flow after water flow post glycerol exposure in 3), during dissolved oxygen flow after water flow post glucose exposure in 4). b) Integrated peak areas for linearly bound CO on 5 wt% Pt/γ-Al_2O_3 over time.

Conclusions

At room temperature and pressure, aqueous phase glycerol and glucose are readily activated over Pt/γ-Al_2O_3 forming surface bound hydrogen and CO. These species are removed by O_2 saturated water. The formation of these surface species from glycerol is faster than from glucose. This is likely due to glucose's being sterically hindered on the Pt surface that cannot be removed by dissolved O_2 in the case of glucose. Glucose also results in more carbonyl species which are resistant to oxidative removal from Pt.

References

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