

Formic Acid as a Hydrogen Source for Vapor Phase Catalytic Reactions

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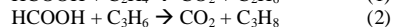
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Introduction

There is currently a great deal of interest in the development of so-called "Second Generation" bio-refining processes, an example being the Biofine Process. This transforms cellulosic biomass feedstock by acid catalyzed hydrolysis to give a mixture of levulinic acid and formic acid (FA) together with a "char" residue [1]. The levulinic acid can be used for the production of chemicals and transport fuel additives. We are currently examining potential uses of the FA produced. For example, FA can be decomposed over a variety of different catalysts to give hydrogen and CO₂; the aim is to find catalysts to optimize hydrogen production with a minimum of CO production.

As part of our study, we have examined the possibility of using FA as a direct source of hydrogen in hydrogenation reactions, thus avoiding the separate step of hydrogen production. To test this idea, we have examined the use of FA in the hydrogenation of ethylene and propylene over a number of catalysts (reactions 1 and 2):



Materials and Methods

Different materials (for example, 10 wt% Pd/C (Degussa), 1 wt% Au/C (WGC), 1 wt% Au/TiO₂ (WGC), 1 wt% Pt/ZrO₂) were tested for both FA decomposition and the direct hydrogenation of olefins (C₂H₄, C₃H₆) by FA. The catalysts were placed in a quartz tubular reactor, then pretreated in a 1% H₂/Ar mixture at 573 K for 1 h and cooled in He to reaction temperature. The reaction products were analyzed by a gas chromatograph.

Results and Discussion

Good results were obtained with a number of catalysts and will be reported. However, only the results for the Pd/C catalyst will be shown here since this material gives the best results obtained for both FA decomposition and the hydrogenation of the olefins. A very small amount of this catalyst (6 mg) gave decomposition of FA to hydrogen and CO₂ at temperatures as low as 358-433 K. Furthermore, C₂H₄ as well as C₃H₆ could be hydrogenated effectively by FA over the same range of temperatures. No deactivation was observed. Complete conversion of the FA was achieved at about 433 K. The undesirable CO production was almost completely eliminated, the selectivity to CO₂ being very high (Fig. 1).

Generally, the products of the Biofine process contain significant amounts of water and so it is important that the FA reactions will occur in the presence of water vapor. It was found that

water vapor has a small positive effect on both FA decomposition (Fig. 1) and C₂H₄ hydrogenation by FA (Fig. 1).

It is suggested that the mechanism involves two important steps: the formation of adsorbed hydrogen from FA and its consumption by the olefin. That the second step is probably fast was shown by the observation that the olefins examined could both be hydrogenated by hydrogen with 100% conversion even at 313 K over the Pd/C catalyst. Thus, hydrogenation by molecular hydrogen is more effective than that by FA, the rate of the latter reaction being determined by the rate of production of surface hydrogen.

Conclusions

It has been shown that olefins can be hydrogenated effectively in the vapor phase by using FA instead of hydrogen. This means that the separate step of hydrogen production as well as the need for hydrogen storage and transportation can be eliminated. It may also be possible to use FA as a hydrogen source for some of the hydrogenation steps in the conversion of levulinic acid to fuel additives and this is being examined. The method may also have applications in other hydrogenation reactions.

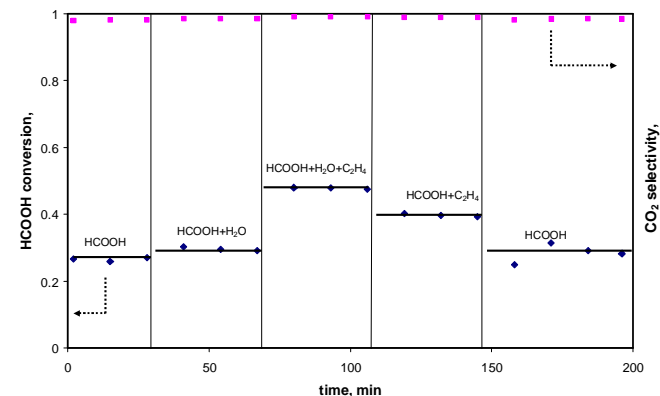


Figure 1. Comparison of the HCOOH conversion and CO₂ selectivity with different gas compositions: (2.4% HCOOH, 2.4% HCOOH/2.3% H₂O, 2.4% HCOOH/2.3% H₂O/1% C₂H₄, 2.4% HCOOH/1% C₂H₄ balance He) over a 10 wt% Pd/C catalyst (total flow rate 51 ml/min, reactor temperature 388 K)

References

- Hayes, D. J.; Fitzpatrick, S.; Hayes, M. H. B.; Ross, J. R. H., The Biofine process - Production of Levulinic Acid, Furfural, and Formic Acid from Lignocellulosic Feedstocks. In Biorefineries-Industrial Processes and Products, Kamm, B.; Gruber, P. R.; Kamm, M., Eds. Wiley-VCH: Weinheim, 2006; Vol. 1, pp 139-164.