SURFACE-LEVEL INVESTIGATIONS OF BENZYL ALCOHOL REACTION ON THIOLATE-COVERED SURFACES

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Abstract

Benzyl alcohol is a significant biomass-derived intermediate from lignin and a useful probe molecule for aromatic oxygenates. During reaction with hydrogen, benzyl alcohol can be converted to benzaldehyde, toluene and benzene. Recently, self-assembled monolayers-coated (SAM-coated) catalysts, which can improve the reaction selectivity through modifying the catalyst surface and blocking non-selective catalytic sites, have recently received attention[1]. Therefore, in this study, we explored the use of thiol SAMs to modify Pd/Al_2O_3 and enhance the selectivity of benzyl alcohol hydrodeoxygenation to toluene, and used surface science techniques to characterize the mechanism.

On uncoated Pd catalysts, after an initial deactivation period, the selectivity to toluene under steady state conditions was less than 35%, and the dominant product was benzene. After the SAM modification, the selectivity to toluene can reach 85% and the production of benzene is remarkably reduced, which shows that the SAMs are effective in enhancing the selectivity to toluene. Remarkably, on surfaces coated with adamantanethiol, both selectivity and overall catalytic activity were improved. Surface science techniques were employed to further investigate this chemistry, with Auger electron spectroscopy (AES) used to confirm sulfur coverage and temperature programmed desorption (TPD) to monitor the thermal chemistry of adsorbates. On octadecanethiol-coated surfaces, the benzene signal disappeared along with the hydrogen peak around 495K indicating reduced decarbonylation activity. Both of these observations indicate that the flat-lying conformation, which was the conformation found to generate benzene[2], was restricted and the production of benzene was thus decreased. In contrast, production of toluene was still observed on the thiol-coated surface, consistent with toluene formation occurring through a more

upright conformation. Thus, the SAM modification strategy could be useful in making production of biomass-derived products more feasible and competitive by lower purification cost and less environmental impact.