



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI  
SHORT ABSTRACT OF THESIS

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Thesis Title: **Enhanced Dehydrogenation of Butane over Supported Pd & Pt Based Catalysts Prepared by Modified Electroless Deposition**

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**SHORT ABSTRACT**

Butenes serve as the essential feedstock for production of many valuable chemicals. Demand and market value of butenes have experienced a surge in recent years. This work investigated the production of butene by dehydrogenation of butane over alumina supported Pd & Pt based catalysts prepared by modified electroless deposition. The effects of variations in catalyst preparation, metal composition, metal deposition sequence, process parameters and addition of surfactant and promoter were studied. In modified electroless deposition, the metal precursor and reducing agent solutions were passed through the porous support sequentially in cyclic steps. Various characterization techniques such as AAS, EDX, XRD, TEM, XPS, TPR, FT-IR and NH<sub>3</sub>-TPD were used to determine the physicochemical properties of prepared catalysts. The catalytic performances of all the prepared catalysts were evaluated in terms of conversion, selectivity, yield and stability for butane dehydrogenation reaction at different temperatures from 100-600 °C under atmospheric pressure in a down-flow fixed bed reactor. The physicochemical properties and catalytic performance of monometallic Pd and Pt catalysts prepared by deposition was compared with that of prepared by conventional impregnation method. The total metal loading was maintained at 112.8 μmole per gram of catalyst for all the samples. The metals were observed to be better dispersed in catalyst synthesized by deposition compared to that prepared by impregnation. The monometallic supported Pt catalyst showed the higher activity at lower temperature, while supported Pd, was more active at temperature above 550 °C. The deposited supported Pd catalyst exhibited higher selectivity towards overall butene formation (>90%) compared to deposited supported Pt catalyst (82%). The addition of surfactant to supported palladium catalyst lowered the average cluster size of deposited metal. Both anionic (SDS) and non-ionic (Tween 20) surfactants were observed to be most effective in dispersing the metals on the support surface. Average Pd metal cluster size obtained for catalyst prepared by impregnation, deposition and SDS surfactant assisted deposition were 11.89, 4.6 and 1.18 nm, respectively. The supported Pd catalyst, prepared in presence of anionic SDS surfactant with the highest metal dispersion showed the best catalytic performance with a conversion of 33% and 99.7% selectivity towards butenes. The co-deposition of 10 mol% of copper or silver with palladium increased activity and yield of butene as well as stability. The copper promoted catalyst showed highest conversion of 34% at 550 °C while, the Ag promoted catalyst possessed highest selectivity towards butenes (>90% at 550 °C). The highest butene yield was 32% when copper content was increased to 20 mol%. The palladium metal was in strong interaction with the promoter metals forming the highly active sites that enhanced the performance of the promoted catalysts. The effect of variation in relative amount of

palladium and platinum in bimetallic Pd-Pt catalysts was studied using co-deposition and impregnation methods. All the bimetallic Pd-Pt catalysts exhibited superior performance compared to that of either monometallic Pd or Pt catalysts and that may be attributed to strong synergistic interaction between the metals, stronger metal-support interaction and lower acidity of catalysts. The lower acidity of bimetallic catalysts resulted in their higher butene selectivity and stability by minimizing cracking and secondary reactions. The ratio of Pd to Pt was varied as 3:1, 1:1 and 1:3 on molar basis keeping the total metal loading constant. The deposited bimetallic catalysts, having equimolar palladium and platinum, showed the highest butane conversion of 48.5% and butene yield of 42% at 550 °C. The metal deposition order of bimetallic catalysts also affected their performance. The co-deposited catalyst with more uniform distribution of Pd and Pt metals showed better performance than bimetallic catalysts prepared by sequential deposition. The co-deposited Pd-Pt/Al catalyst showed the highest butane conversion of 50% at 600 °C and maintained a highest stability with only 15% deactivation after reaction time of 10 h. The same catalyst showed highest butene yield of 44% at 525 °C. Further, the effects of various process parameters on butane dehydrogenation reaction were investigated over best performing co-deposited Pd-Pt/Al catalyst. The activation energy for butane dehydrogenation reaction was determined to be 103 kJ/mol. The present study established the superior performance of catalysts prepared by modified electroless deposition method. This deposition method resulted in better metal dispersion and higher metal-metal interaction on support surface in comparison to impregnation. Palladium proved to be equally active component for butane dehydrogenation with better stability and selectivity compared to Pt. Effectiveness of anionic and non-ionic surfactants in dispersing depositing metals and thereby increasing performance of catalysts was observed. Equimolar co-deposited Pd-Pt bimetallic catalyst evolved as the most active catalyst for butane dehydrogenation in present study, giving butene yield of 42%, higher or at par with that reported by many of the studies for dehydrogenation.