

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

The results of this study clearly show that the method of catalyst preparation has great influence over the metal dispersion and adsorption behavior. Coimpregnation of the Al_2O_3 support with platinum and small amounts of tin facilitates the formation of high Pt dispersion, exceeding the dispersion of monometallic Pt/ Al_2O_3 catalysts with similar Pt loading. However, sequential impregnation of the Al_2O_3 support with Sn first, followed by Pt, leads to low Pt dispersion, as evidenced by consistently lower H/Pt and O/Pt ratios as compared to coimpregnated catalysts with similar overall Pt and Sn loading.

The O/Pt ratios obtained are consistently higher than the H/Pt ratios, showing a trend towards increasing O/Pt ratios with increasing Sn content. It appears that oxygen adsorbed on highly dispersed platinum particles can migrate from the platinum sites to adjacent tin sites, populating the Sn surface. Sn is in a state of Sn(II) and/or Sn(IV), according to XPS results.

On the monometallic Pt/ Al_2O_3 catalyst, the pulse chemisorption method used here gives lower uptakes of hydrogen and oxygen compared to static volumetric methods. These differences reflect the significant amount of weakly held hydrogen that can be removed by evaluation after static volumetric chemisorption. Oxygen, on the other hand, tends to be strongly adsorbed and cannot be removed by evacuation. In the static volumetric method, the atomic ratio of adsorbed oxygen to adsorbed hydrogen $O_{\text{ads}}/H_{\text{ads}}$ was 0.73. In the pulse chemisorption method, the ratio was 0.71, showing good agreement between the two methods.

Comparing static volumetric chemisorption data for the coimpregnated catalyst series to the pulse chemisorption data shows agreement in the qualitative trends. For example, in both cases the O/Pt ratio increases with Sn content. However, the static method gives slightly higher O/Pt ratios. In the case of hydrogen adsorption, the H/Pt ratio goes through a maximum for the catalyst with 0.1 wt% Sn. Again, the static volumetric data show slightly larger hydrogen uptakes. These differences in gas uptake can be attributed to the different equilibration times. In the static experiments, it is likely that the overall gas uptake measured includes weakly

adsorbed species, which are removed by the carrier gas stream during pulse chemisorption experiments.

During TPD of methanol from bimetallic Pt-Sn/Al₂O₃ catalysts, methanol decomposed primarily into hydrogen and carbon monoxide. Hydrogen desorbed first, while the desorption of carbon monoxide occurred at higher temperatures. In the coimpregnated catalyst series, the desorption peaks of both H₂ and CO were gradually shifted to higher temperatures with increasing Sn content. In the sequentially impregnated catalyst series, the same shift to higher desorption temperatures was observed for all Sn containing samples, except for the catalyst containing 5% Sn, where the shift was significantly larger than on all other samples. The temperature difference between the H₂ and CO desorption peak maxima increased systematically with increasing Sn content in both catalyst series. This study has demonstrated that the adsorption and decomposition behavior of methanol on platinum is strongly modified by the presence of tin. The relative distribution of Sn to particles of different size and nature, such as alloy particles or partially oxidized Sn species interacting with the alumina support) influences the strength of adsorption of both H₂ and CO.

In the methanol oxidation study, the alumina-supported monometallic Pt catalyst was found to be the most active methanol oxidation catalyst. The trend in oxidation temperature was similar to the maximum peak temperature as seen from the TPD results. The main carbon-containing products of methanol oxidation over the alumina-supported monometallic Pt and bimetallic Pt-Sn catalysts were found to be CO₂ and methyl formate (CH₃OCHO). A small amount of tin can counteract the deactivation of platinum catalyst.