CHAPTER II

LITERATURE REVIEW

The process of the formation of a supported nickel catalyst obtained by reduction in hydrogenation of nickel chloride heterogenized in silica was studied by Stakheev et al. [1] and found that no direct dependence between metal dispersion and metal content in the range 0.8-4.6 wt.% of nickel. An increase in the reduction temperature from 250-360 °C resulted in growth of the average diameter of nickel particles from 4.0 to 8.0 nm. Disperse nickel was prepared by impregnating alumina supports of different pore-morphologies have been observed by Kircha and Kolter and Riedert [5], kinetic of reduction of Ni^{2+} compound is controlled by nucleation of the metallic phase, leading to preferential formation of large crystallities of the metal at lower temperature

Ishiyama et al. [6] have perpared a high dispersed nickel-alumina catalyst by sol-gel process using hydrous alumina sol derived from an aluminum salt solution. The size of nickel particles is controlled by the dimensions of the network of the homogeneous percursor alumina gel. This new catalyst shows higher selectivity in liquid phase hydrogenation of 1,3 and 5,5-cyclooctadiene than either raney nickel and impregnated nickel-alumina catalyst. Ryczkowski [7] have studied preparation technique for nickel on r-alumina catalyst, double impregnation technique was used for highly dispersed nickel. In benzene hydrogenation reaction of this catalyst have high turnover number (TON), good stability and easy regeneration.

Chen [8] have observed the pH level of nickel nitrate solution for impregnation. Its influenced change a peak of temperature-program reduction (TPR), a peak of temperature-program desorption (TPD) and particle size of supported nickel.

The effect of post-impregnation drying condition on the physical properties and overall rate of benzene hydrogenation were investigated with nickel/alumina catalysts studied by Uemera and Yoshimitsu [2]. Uniform nickel concentration profiles were obtained with the adsorptive support independent of the drying conditions, but the reduction degree of nickel by hydrogen and the nickel particle diameter were influenced by the drying conditions. With the nonadsorptive support, the drying conditions have significant effect on the nickel profiles. In this case, the reduction degree and particle diameter are dependent on the local total-nickel (reduced and unreduced nickel) content. The pore experimental results of the overall reaction rate of benzene hydrogenation were found to be consistent with the change of the pore structure. The nickel profile have been studied by Uemura [9] of impregnated nickel/alumina catalyst by applying a wide range of drying condition and found that the fraction on migrated Ni^{2+} increases as the drying rate increases.

Interaction of nickel ions with a r-alunima support have been studied by De Bokx et al. [10] and found that in calcined sample of low nickel content, nickel is present exclusively as a "suface aluminate" with higher metal loadings a separate NiO pahse was deteched. From potentimetric titration experiments it was concluded that a percursor of the surface spinel, viz, a mixed hydroxide surface compound, is already formed in aqueous solution.

Hoang-Vaw [11] have characteried nickel catalysts by chemisorption Techniques and found that the series prepared from nickel nitrate, alumina support gave the highest dispersions of nickel, which varied only slightly with the reduction temperature, whereas the dispersion of titania-support catalysts decreased significantly when the reduction temperature was increased. In contrast, the series prepared with nickel chloride always exhibited low exhibited low metal dispersions which were nearly independent of the nature of the support and the reduction temperature.

Marecot et al.[12] have shown that benzene hydrogenation at a low temperature under atmospheric pressure must be considered as a structure-sentsitive reaction. Pulse measurements show that two type of benzene adsorption occur: a non-reactive form which remains adsorbed on the catalyst wihtout reaction and a reactive on which is hydrogenated. Specific activity of benzene relate with weakly bound hydrogenation and reactive adsorbed benzene. Dispersed of nickel metal on support increases weakly bound hydrogen.

Hydrogen adsorption of supported nickel catalysts have been studied by Gordon [13]. The number and population of adsorption states at moderate to low coverages and heats of adsorption were found to be strong function of the support. Hydrogen adsorption on nickel alumina was found to be an activated process. Reduction of nickel titanium oxide at high temperatures (600-700 °C) was observed to strongly suppress the adsorption of hydrogen.

Mirodatos et al.[14] have studied the benzene hydrogenation reaction over nickel catalyst at low temperature (below 400 K). Rate of reaction is $k_0 e^{Eo/RT}(1-O_H)^x P_H P_B{}^E$. The rate-limiting step can be described as a two-body process between: (1) the active site, and ensemble of about four adjacent nickel atom occupied by a chemisorbed benzene molecule. (2) a molecular hydrogen species.

Ceckiewicz and Dehuon [15] have observed mixtures of 0.6% Pt/r-Al_2O_3 and r-Al_2O_3, with ratio 1:20, give specific activity increase about fourfold. The results suggest that benzene hydrogenation occurs on both Pt/r-Al_2O_3 and the diluent r-Al_2O_3.

Bertolini [16,17] have studied of two surface state have been evidenced on PtNi(110) depending on the equilibration temperature. The low temperature equilibrated sample looks like PtNi(111), but high temperature stabilized sample shows different surface electronic properties and an enhanced reactivity. The surface structure inside the (111) face of two substitution alloys. $Pt_{0.5}Ni_{0.5}$ and $Pt_{0.78}Ni_{0.22}$ was investigated by LEED. In both cases we find an important compositional oscillation across the three outermost layers. The concerned Pt concentration (at%) are 88±2, 9±5 and 65±10 for $Pt_{0.5}Ni_{0.5}$ and 99±1, 30±5 and 87±10 for $Pt_{0.78}Ni_{0.22}$. This oscilation is a new and important element to be accounted for in the discussion of the specific chemisorptive and catalytic properties, particularly as regards the hydrogenation of 1,3-butadiene.

Gaerriro [18] have used of hydrogen-oxigen titration method to characterize platinum-nickel support catalyst has shown that the number of oxidized or reduced nickel layers is dependent on the atomic composition. This phenomenon involves dynamic changes of the surface probably by spillover

Bonnier et al. [3] have studied Ni-Cr and Ni-Mo catalyst by co-reduction of dry iodied of appropriate composition with sodium naphthalene as reducing agent, this procedure give finely divided homogeneous alloys. The bimetallic powders developed a large BET surface area. For acetophenone hydrogenation, Ni-Cr catalyst exhibited catalytic activity greater than commercial Raney nickel and showed better selectivity, the yield of 1-phenyethanol being as high as 95%. Ni-Mo catalysts wwere approximatly as reactive as commercial Raney nickel, with an increase the rate of hydrogenolysis of the C-OH bond.

Small amounts of platinum incorporated in alumina-supported nickel catalysts have been ovserved by Novak and Koros [19], to enhance activation of the nickel by hydrogen. Hydrogenolysis reactions of n-heptane with hydrogen were used to characterize the catalytic activity. Platinum to nickel atomic ratios as low as $5x10^{-3}$ were sufficient to cause several-fold increases in the extent of conversion compared with the nickel component. These large effects appear to be due to precious metal catalyzed hydrogen reduction of supported nickel oxide.

The catalytic activity of alumina-supported platinum-nickel alloys has been studied by Renouprez et al. [20]. A strong maximum in the turnover for the isomerization of neopentane to isopentane was observed in the composition range (Pt 80-90 - Ni 20-10). Similarly, the rate of hydrogenolysis of neopentane is increased by two orders of magenitude for the composition $Ni_{90}Pt_{10}$. This synergistic effect was attributed to modifications of the electronic properties of both metals at the two critical compositions.

Dominguez [21] have concluded that the structure of these platinum-rich alloys, (i.e., Pt_{78}-Ni_{22}/C) is comprised mainly of cubo-octahedral particles and of a smaller proportion of irregular, triangular and square shapes. Nickel-rich alloys,(i.e., $Pt_{12}Ni_{88}$/C), exhibit many irregular shapes and a lower proportion of special and five fold decahedral and icosahedral shapes.