CONCENTRATION PROFILES OF SUPPORTED BIMETALLIC CATALYSTS

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Abstract: This study relates to the movement of Zr+4, Co+2, Rh+3, Ir+3 and Mo+3 ions relative to Ni+2 ion when impregnated on gamma alumina cylindrical pellet (dia. 2.5 mm). In general, with the increase in soaking time and at higher solution concentration, the metallic ions penetrated deep into the pellet. The preferential adsorption of ions of Zr+4, Co+2, Ir+3 and Mo+3 at the periphery with respect to ions of Ni+2 is due to higher ionic charge density on these ions, whereas the restricted movement of Zr+4 ion, besides higher ionic charge, is also due to its bigger ionic radius.

Keywords: Additive ions, nickel ions, gamma alumina pellet, soaking time, solution concentration, charge density, ionic radius

Introduction

Supported bimetallic catalysts are very important for chemical processing industry. These are usually prepared by impregnation technique. Since, the concentration profile of the active component affects the durability and performance of the catalyst, attempts have been made to predict and control the distribution of active metal ions inside the porous support. Extensive work has been carried out to suggest that initial distribution of solute in the porous solid depends on its adsorption characteristics [1], adsorption rate, equilibrium adsorption coefficient of impregnate on pore wall and relative capacity of wall for adsorption [2], pH [3] and concentration [4] of the impregnating solution, the nature of starting material [5], the presence of other ions [6] and soaking [7] and drying time [8]. All these studies pertain to the movement of ions of one metal. The information regarding simultaneous distribution of ions of two metals in the porous support is scanty. Fierro et al. [9] while determining the Co and Mo concentration profiles in gamma alumina extrudates observed that incorporation of these two ions in one single step produced degenerated shell profiles for both Co and Mo atoms. Their relative initial distribution was related to their respective initial concentration. The stability of the surface anion pairing is enhanced by increasing the charge and size of the adsorbed anion [9]. In this study, we have attempted to find the movement of the additive (Zr+4, Co+2, Rh+3, Ir+3 and Mo+3) ions relative to the nickel ions in gamma alumina.

Materials and Methods

Equimolar (3.4 % metal ion) solution each of Ni – Zr, Ni-Co, Ni-Rh, Ni-Ir and Ni-Mo was prepared by dissolving respective nitrates in distilled water. One gram of gamma alumina pellets (Al – 0104 T 1/8 Lot 72, Harshaw Chemicals, surface area 350 m²/g, dia 2.5 mm and pore size 62 Å), was immersed in 10 ml of each solution separately for eight, sixteen, twenty four and seventy two hours. The pellets after the intended immersion time were taken out and

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dried in oven at 105°C. The dried pellet was embedded in thermoplastic resin and its cross section was exposed by grinding with sand paper (No. 220, 600 and 1500). Fine diamond powder polishing agent was employed for fine finishing of the exposed cross sectional surface. It was coated with a layer of carbon by vacuum deposition.

The concentration (the ratio between number of atoms of metal M and that of Aluminum within beam spot size 10 µm) of the metallic ions of Ni^{+2} and respective additives along the diameter were measured by electron probe micro-analyzer (JEOL JSM-35 CF/DDS/LINK– 860/2), located at PINSTECH Nelore, Islamabad. The acceleration voltage of electron beam was 15kv and scanning speed was adjusted at 0.02 mm/min. The analyzer provided the computed results.

Results

The alumina being the support, the results are presented as M/Al ratio, the number of atoms of metal and that of aluminum within beam spot size (10 µm), versus radial fraction. The concentration profiles for various soaking time are given in Figs. 1 to 5. Simultaneous impregnation of Ni^{+2} and Co^{+2}, at various initial concentrations, produced concentration profiles which tended to become flat and uniformly distributed with increasing soaking time. With low initial solution concentration, the solute was adsorbed more strongly towards the edge. The profiles of Ni^{+2} and Mo^{+3} indicate higher concentration near the periphery. However, at higher soaking time, Mo^{+3} ions moved further towards the centre. Ni^{+2} ions in this case were also evenly distributed. The co-impregnation of Ni^{+2} and Zr^{+4} showed a similar pattern as that of Ni^{+2} -Mo^{+3} except that Ni^{+2} ions in competition with Zr^{+4} ions gave more flat profile as compared to Ni^{+2} ions in competition with Co^{+2} or Mo^{+3} ions. A different picture emerges when Ni^{+2} and Rh^{+3} ions were impregnated. The shape of the profile and concentration for both the ions was similar. In fact, they superimposed each other. These profiles became more flat and uniformly distributed with increase in soaking time. Ni^{+2}-Ir^{+3} system showed a profile wherein Ni^{+2} ions appeared to move uniformly, below the profile of Ir^{+3} ions. However, with longer soaking time, the profiles of Ni^{+2} and Ir^{+} ions superimposed each other.

Discussion

This study aimed to evaluate the following three aspects.

a. The effect of soaking time.

b. The effect of initial solution concentration.

c. The competition between two metallic actions.

The Effect of Soaking Time

The concentration profiles (Figs. 1 to 5) indicate that metallic cations move into centre with increasing soaking time, resulting in a decrease in concentration gradient. These results are not unexpected. Cervello et al. [10] investigated the impregnation of dry and wet gamma alumina pellets with nickel solution and observed that short contact time renders uniform or egg shell catalyst, while longer soaking time increases the surface concentration of the adsorbed nickel and produces a more uniform catalyst distribution. Fierro et al. [9] analyzed several Mo-profiles obtained either at short or longer impregnation time. It was concluded that irrespective of the initial solution concentration, the Mo-profiles almost leveled off at the longer impregnation time, whereas a shorter soaking time gave profiles which decreased towards the interior of the pellet. The results obtained in this study are in agreement with these findings. It is therefore concluded that soaking time influences the shape as well as the loading of the metallic cations. The cations deposit more near the periphery and travel less into the interior when impregnation time is short. With longer soaking
time the profiles become flat and metal cations are more uniformly distributed.

**The Effect of Initial Solution Concentration**

This aspect was studied in respect of Ni$^{+2}$-Co$^{+2}$ impregnation on gamma alumina (Fig. 1). It was observed that loading of metal cation decreases with decrease in concentration. The profiles follow a parallel trend. Fierro et al. [9] impregnated Mo$^{+3}$ and Co$^{+2}$ simultaneously. The Co-profile was below the Mo-profile because Co concentration was less than that of Mo$^{+3}$. Chen and Anderson [11] impregnated gamma alumina spheres with known amount of chromium and copper compound solutions of different concentration. The dried and calcined spheres were sectioned and concentration profiles were determined along the diameter of circular cross section by an electro probe micro-analyzer. They concluded that the concentration profiles were a function of the solute and the concentration as well as the amount of solution. Komiyama et al. [4], while impregnating gamma alumina sphere with NiCl$_2$ and HNO$_3$, observed that NiCl$_2$ concentration controls the profiles and loading at the core. The profiles show a strong dependence on the initial NiCl$_2$ concentration. Our findings are in good agreement with those observed by Chen and Anderson [11] and Komiyama et al. [4].

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**Figure 1.** Simultaneous impregnation of Ni$^{+2}$ & Co$^{+2}$ on Al$_2$O$_3$. Soaking time: (a) 8 hr, (b) 16 hr, (c) 24 hr, (d) 72 hr. Initial concentrations of co-impregnated solutions: Ni-1 and Co-1, 0.1 mol; Ni-2 and Co-2, 0.05 mol, and Ni-3 and Co-3, 0.025 mol.
Figure 2. Simultaneous impregnation of Ni$^{2+}$ and Mo$^{3+}$ on Al$_2$O$_3$.
Soaking time: (a) 8 hr, (b) 16 hr, (c) 24 hr, and (d) 72 hr.

Figure 3. Simultaneous impregnation of Ni$^{2+}$ & Zr$^{4+}$ on Al$_2$O$_3$.
Soaking time: (a) 8 hr, (b) 16 hr, (c) 24 hr, and (d) 72 hr.
Figure 4. Simultaneous impregnation of Ni^{2+} and Rh^{3+} on Al2O3. Soaking time: (a) 8hr, (b) 16hr, (c) 24hr, and (d) 72 hr.

Figure 5. Simultaneous impregnation of Ni^{2+} and Ir^{3+} on Al2O3. Soaking time: (a) 8hr, (b) 16hr, (c) 24hr, and (d) 72 hr.
Competition between Metal Ions

The solution contained three ions which were Ni\(^{2+}\), one of the additives (Co\(^{2+}\), Mo\(^{3+}\), Zr\(^{4+}\), Rh\(^{3+}\) or Ir\(^{3+}\)) and NO\(_3\)\(^{-}\). The concentration of metal ions was equimolar. The effect of pH, temperature, concentration of nitrate ions or viscosity was assumed to be the same for both metal ions as the solution was homogeneous. It is, thus, an inherent characteristic of the metal ions which are responsible for divergence in the shape of the profiles. As the dry pellets of gamma alumina are immersed in an excess amount of the solution, the solution penetrates the pellets to fill the pores by capillary action. The concentration gradient pushes more ions into the pore. One fraction of these ions is adsorbed at the pore walls while the other fraction remains in solution. The adsorption of ions on the pore wall and diffusion of the ions into the pellet is competitive. It depends, among other factors which being constant in this study, on ionic charge density \([12]\) and ionic radius of the individual ion. Co\(^{2+}\), Mo\(^{3+}\), Zr\(^{4+}\), Rh\(^{3+}\) or Ir\(^{3+}\), the highly charged ions in comparison to Ni\(^{2+}\), get preferentially adsorbed at the periphery. The length of ionic radius can cause the partial exclusion phenomena. If its size is smaller than the pore, it will be excluded (pushed away) from the pore. In case the ionic radius is bigger than the pore radius, exclusion will be due to geometric effect, whereby ions will not enter the pore. The average pore size of Al\(_2\)O\(_3\) pellets used in this study was 62 Å, some pores being bigger while some smaller than the average pore size. The higher ionic content at the periphery of any one of Co\(^{2+}\), Mo\(^{3+}\), Rh\(^{3+}\), Zr\(^{4+}\) or Ir\(^{3+}\) with respect to Ni\(^{2+}\), primarily, would be expected to be due to their higher electron density. Moorthyiedath [13], while comparing Co/Ru ratios in bulk and at the surface, observed that Co/Ru ratio at the surface stays less compared to that in the bulk, whereas considering Co/Si and Ru/Si, more Ru\(^{3+}\) stays at the surface. Dalama et al. [14] concluded in their study that complexing agents change the nature of the charge on the impregnating metal ion to influence its adsorption on the support. This confirms our reasoning that Ru\(^{3+}\), having higher charge density than Co\(^{2+}\), moves less in bulk. In the case of Zr\(^{4+}\), the higher concentration of Zr\(^{4+}\) at the periphery was also due to restricted movement of Zr\(^{4+}\) ions because of bigger ionic radius. Shiau and Tsai [15] prepared Cu/α-Al\(_2\)O\(_3\) by electro-less and impregnation techniques and observed severe blockage of pores in the case of the impregnation method. The shape of the profile indicated that the distance which Ni\(^{2+}\), Co\(^{2+}\), Mo\(^{3+}\), Rh\(^{3+}\), Zr\(^{4+}\) or Ir\(^{3+}\) ions have diffused into the pellet bears some relationship with the respective ionic radius. Mo\(^{3+}\) and Zr\(^{4+}\) because of bigger ionic radii than Ni\(^{2+}\) produced sharp profiles and moved less towards the centre, whereas Ni\(^{2+}\), Co\(^{2+}\) Rh\(^{3+}\) and Ir\(^{3+}\) had flat profiles and penetrated deep into the centre. Raymonde et al. [16] prepared Pt/Pd/α-Al\(_2\)O\(_3\) by micro-emulsion and found it similar to those prepared by the conventional impregnation method. The Pd concentration was low in the bulk as Pt has higher charge density.

References


