CHAPTER 6

STUDY OF INTERACTION BETWEEN SMALL PARTICLES

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6.1 Introduction

The study of physical and chemical properties of microclusters of materials and the variation of these properties with respect to the bulk values have become a focus of considerable attention in recent years (1). Chemical reaction studies provide a useful probe into the structural make up of clusters and also yield information regarding the mechanism of breaking and making of chemical bonds on the cluster surfaces (2). Parant and McElvany (3) obtained evidence for two structural forms of carbon cluster ions, from their differing reactivity with HCN. Reaction studies of Fe and Co clusters with \( \text{N}_2 \) have shown sharp variations in reactivity with cluster size (4). Reaction studies on a variety of transition metal clusters have revealed that chemisorption of \( \text{D}_2 \) occurs with dramatic sensitivity to cluster size in the case of iron, cobalt and niobium clusters whereas Cu clusters are found to be completely unreactive to \( \text{H}_2 \) chemisorption (5). Time of flight mass spectrometric study of reaction of iron clusters with an excess of hydrogen have shown the formation of fully hydrogenated product \( \text{Fe}_n\text{H}_n \) whose composition remain fixed over a wide range of hydrogen pressures (6). During the past
years considerable attention has been given to the effect of metal support interactions on the chemisorptive and catalytic properties of the metal phase (7). The properties can be influenced by electron transfer or by chemical bonding between metal particles and the support. Tauster et al (8,9) have experimentally shown the possibility of strong metal support interactions. Strong chemical interaction between metal and substrate has also been reported in the case of Ni, Pd and Pt with carbon (7). Now there is increasing evidence for strong interactions between transition as well as nontransition metal oxides with metal.

The interactions involving metal clusters can be characterized as either surface chemisorption reactions or bulk reactions (2). In the former, reactions involve the formation of surface adsorbate bonds which are either physical or chemical. Bulk reactions are characterized by a more extensive breakage of metal-metal bonds and the formation of a bulk compound having metal-non metal bonds. The chemisorption reactions of Fe clusters with ammonia and water and that of nickel clusters with ammonia have been reported by Riley (2). These reaction studies represent fundamental chemical processes that are promoted by the interaction between adsorbate and metal atoms and an
understanding of their detailed sequence of steps will provide us valuable information about the unique properties of metal surfaces. Chemisorption and chemical reaction studies on size selected clusters have made possible the estimation of activation barriers for chemisorption on the cluster surfaces (11).

Although chemisorption reactions of clusters have been studied in detail, the possibility of bulk reactions between clusters of different materials has not been investigated extensively. When clusters of different materials interact, the product of interaction has to be analysed to determine the nature and extent of interaction. The product of interaction can be analysed using electron and X-ray diffraction to establish the identity of the product. EDAX can effectively be used to determine whether the interaction is stoichiometric or not and vibrational spectroscopy may be made use of to see whether the expected frequencies are present. The study of interaction between microclusters of Ag and As₂S₃, and that between AgI and HgI₂ using electron diffraction, X-ray diffraction and EDAX are included in this chapter. In chapter 9 the study of the nature and extent of interaction between microclusters of AgI and HgI₂ using laser Raman spectroscopy is discussed.
SECTION 1

6.2 Interaction between Microclusters of Silver and Arsenious Trisulphide

6.2.1 Introduction

Freundlich and Moor (10) had studied the interaction between silver and As$_2$S$_3$ suspensions and the possibility of formation of the compound Ag$_3$AsS$_3$ had been indicated by them. The author reports here the study of the feasibility of bulk chemical reactions between microclusters of silver and arsenious trisulphide, using electron diffraction and EDAX. The results of the study show that bulk interaction between these clusters are highly probable and also considerable chance is there for the formation of complexes.

6.2.2 Experiment and Observation

Aqueous suspensions of silver (11) used for the present study were prepared as discussed in section 1 of chapter 4. Concentration of silver suspension thus prepared was 0.129 gm/litre. Arsenious trisulphide suspension of concentration 0.6888 gm/litre was prepared by a chemical method (12) as discussed in section 3 of chapter 4. The two suspensions are allowed to interact by titrating the suspension of arsenious trisulphide against the suspension of silver until precipitation occurs. This precipitate
which may contain $\text{Ag}_3\text{AsS}_3$ or complexes between Ag and $\text{As}_2\text{S}_3$ particles as the product of interaction, and unreacted Ag and $\text{As}_2\text{S}_3$ particles, was separated, washed repeatedly with distilled water and redispersed in distilled water. The clusters of Ag, $\text{As}_2\text{S}_3$, and that of the product of interaction are subjected to TEM and selected area electron diffraction studies by placing a drop of the respective suspensions on the grid of the Philips EM 301 TEM and allowing the liquid phase to evaporate off. From the TEM micrographs (refer Figs 4.2 & 4.11) the average particle size is found to be about 10 nm for Ag and 8 nm for $\text{As}_2\text{S}_3$ clusters respectively. The electron diffraction pattern of Ag and $\text{As}_2\text{S}_3$ clusters are found to be spotty (refer Figs 4.3 & 4.12) whereas that of the product of interaction shows diffused and broadened rings (Fig.6.1) with reflection corresponding to unreacted Ag. The interplanar spacing calculated for Ag and $\text{As}_2\text{S}_3$ clusters indicate a lattice contraction (refer section 1 and 3 of chapter 4). A portion of the precipitate was subjected to X-ray analyses and the diffraction pattern (Fig. 6.2) was found not to contain any sharp peaks indicating the absence of crystallinity. Chemical analysis of different samples of the precipitate was done by EDAX. The atomic percentage of Ag, S and As do not indicate stoichiometric reaction in any of the cases. A typical EDAX result is given in Table 6.1.
Fig. 6.1 Electron diffraction pattern of aggregates of particles of the product of interaction between small particles of Ag and As$_2$S$_3$. 
Fig. 6.2. X-ray diffraction pattern of the product of interaction between clusters of Ag and As$_2$S$_3$. 
Table 6.1 EDAX Results

<table>
<thead>
<tr>
<th>Elements</th>
<th>Atomic %</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>58.910</td>
<td>74.783</td>
</tr>
<tr>
<td>S</td>
<td>21.699</td>
<td>8.136</td>
</tr>
<tr>
<td>As</td>
<td>19.391</td>
<td>17.081</td>
</tr>
</tbody>
</table>

6.2.3 Discussion

Since small clusters are composed predominantly of surface atoms, their chemical properties may well reflect the macroscopic details of surface activity. It has been observed that in many cases the activity of a surface is highest at steps and other faults where the bonding is presumably strained (13), as would be expected for small clusters, which are under a surface stress due to high surface to volume ratio. It has been shown through electron diffraction studies in the case of fine particles of platinum and gold that a decrease in the lattice parameter occurs which is proportional to the reciprocal of the particle size and that this lattice contraction is an evidence for the existence of a surface stress (14,15). The electron diffraction photographs of Ag shows a lattice contraction as discussed in section 1 of chapter 4. The d values calculated in the case of As$_2$S$_3$ also indicate a
lattice contraction when compared with the ASTM values. It may be expected that both Ag and As$_2$S$_3$ clusters are in a state of surface stress and naturally there may be a tendency to release the resultant strain. As a result, when suspensions of clusters of Ag and As$_2$S$_3$ are brought into contact, in addition to the mutual or co-precipitation of the suspensions, a chemical reaction may ensue between them, which may release the strain. The clusters of Ag and As$_2$S$_3$ when meet together, there may be a diffusion of atoms constituting the Ag and As$_2$S$_3$ clusters into each other, and a rearrangement of atoms and the establishment of metal non-metal bonds may occur, leading to the formation of a cluster of a compound of the two clusters, instead of forming surface adsorbate bonds as in the case of chemisorptive reactions. The compound cluster in all possibility may contain a stoichiometric compound Ag$_3$AsS$_3$ as well as some unreacted interactants. The study of formation of Pd-C phase through the interaction of palladium black with ethylene, acetylene or carbon monoxide has revealed that the reaction process involves the deposition of a carbonaceous overlayer on Pd followed by an activated diffusion of carbon atoms through the metal lattice (16). Also reaction studies of Fe clusters with an excess hydrogen to yield fully hydrogenated products have shown that the Fe clusters probably have a specific configuration, the one having least free energy,
and the iron substructure because of the diffuse nature of metal-metal bonding, rearranges during hydrogenation so that in the hydride it differs from that in the bare metal clusters (6). The mechanism of interaction between Ag and As$_2$S$_3$ clusters may also be considered to be similar to those discussed above. The electron diffraction pattern of the product of interaction exhibit a strong broadening of the diffraction rings and the rings are also observed to be diffused. A similar strong broadening of the diffraction lines of carbon supported palladium was reported by Anton and Poppa (17). This broadening indicates a higher degree of disorder within the particle lattice (18). In the case of clusters of the product of interaction some disorder is present due to the presence of the unreacted part. This result is substantiated by the amorphous-like X-ray diffraction pattern of the product of interaction (Fig.6.2). The microdiffraction pattern observed for chemisorptive metal support interactions in the case of chemisorption of carbon on crystalline Pd particles reveals that the crystalline nature of the Pd particles remains without distortion even after the chemisorptive reactions (18). The appearance of diffused and broadened ring pattern (Fig.6.1) shown by the reaction products of Ag and As$_2$S$_3$ in sharp contrast with the electron diffraction patterns shown by Ag and As$_2$S$_3$ (see Fig 4.3 and 4.12 of chapter 4)
indicates that the reaction may not be purely chemisorptive. A few diffraction spots are present in the electron diffraction pattern of the product of interaction, indicating the presence of some unreacted Ag clusters. The EDAX results of different samples of the product of interaction show that the percentage of various elements in the reaction product are not consistent with those of a stoichiometric compound. Thus it may be inferred that the interaction between Ag and As$_2$S$_3$ leads to composite clusters each of which consist of a stoichiometric compound or some complexes of Ag and As$_2$S$_3$ or both, and unreacted Ag and As$_2$S$_3$.

SECTION 2

6.3 Interaction between Small Particles of AgI and HgI$_2$

6.3.1 Introduction

Even though the interactions of clusters of a metal with a gas (6, 13), a non-metal or a compound (16,19) have been investigated in detail, that between clusters of two compounds has not been reported. In section 1 of this chapter interaction between a metal cluster and a compound
cluster was discussed while in this section the interaction between two compound clusters, namely, AgI and HgI₂ is discussed.

6.2.2 Experiment and Observation

The pale yellow suspensions of AgI and red suspension of HgI₂ clusters in water prepared as discussed in section 2 of chapter 4 were mixed quickly with vigorous stirring. The microclusters interacted producing a yellow precipitate which may probably be Ag₂HgI₄ or some complexes between AgI and HgI₂. The precipitate was washed repeatedly with distilled water and redispersed in water. The suspensions of AgI, HgI₂ and the product of interaction were subjected to TEM, electron diffraction, X-ray diffraction and EDAX studies. The average size of the AgI, HgI₂ clusters and that of the product of interaction were found to be 23nm, 30nm and 48nm respectively. Electron diffraction patterns of AgI and HgI₂ (refer Fig. 4.7 to 4.10 of chapter 4) were found to be spotty rings while that of the product of interaction (Fig 6.3) shows diffused and broadened rings. The X-ray diffraction pattern of the product of interaction is shown in Fig 6.4. A typical EDAX result is given in Table 6.2
Fig. 6.3 Electron diffraction pattern of aggregates of particles of the product of interaction between small particles of AgI and HgI₂.
Fig. 6.4. X-ray diffraction pattern of the product of interaction between small particles of AgI and HgI$_2$. 
Table 6.2 EDAX Results

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>2.535</td>
<td>3.256</td>
</tr>
<tr>
<td>Hg</td>
<td>24.123</td>
<td>16.663</td>
</tr>
<tr>
<td>I</td>
<td>73.342</td>
<td>80.081</td>
</tr>
</tbody>
</table>

6.2.3 Discussion

The study of interaction between Fe clusters and hydrogen by Parks et al has revealed that the iron substructure probably has a specific configuration, the one having lowest free energy (6). Solliard et al have (15) shown that for both gold and platinum a decrease in the lattice parameter occurs which is proportional to the reciprocal of the particle size. This lattice contraction shows the existence of a state of surface stress. Vasserman and Vermaak (20) also have shown that small particles are under a surface stress and that there is a correspondence between surface stress and surface tension values indicating that the observed lattice contraction in small particles is a real physical phenomenon associated with surface properties of the clusters. In our study an estimation of the interplanar spacing (d) from electron diffraction patterns shows that both AgI and HgI₂ clusters are under a surface stress as indicated by a contraction in the d values and it
may be inferred that both these types of clusters possess excess surface free energy. Hence when the clusters are allowed to interact, there is a tendency for them to coalesce, since this process may reduce the surface free energy. The actual interaction between the AgI and HgI₂ clusters through the rupture of existing bonds and the establishment of new bonds may be a secondary process after the coalescence. The formation of Ag₂HgI₄ or complexes between AgI and HgI₂ depends on the diffusivity of the ions comprising the clusters into each other. Direct evidence for the strong interaction between platinum and SiO₂ on heating Pt/SiO₂ system at 823K is provided by the appearance of new diffraction rings corresponding to the inter metallic compounds in addition to those of platinum in the electron diffraction diagram (20). In the present study the electron diffraction pattern of the product of interaction consists of diffused and broadened ring system which are totally different from that of AgI and HgI₂. This is indicative of the fact that the lattice of both AgI and HgI₂ have been shattered and a re-arrangement of bonds have taken place. The X-ray diffraction analysis of the product of interaction shows a diffraction pattern almost equivalent to the X-ray diffraction pattern of crystalline Ag₂HgI₄ (Table 6.2). In addition, diffraction peaks characteristic of AgI and HgI₂ are also present. This indicates that unreacted AgI and HgI₂
are also present in the compound cluster produced by the interaction. The EDAX analysis of the product of interaction (Table 6.2) showed that the percentage of various elements in the reaction product are not consistent with those for the stoichiometric product Ag₂HgI₄. This also indicates that unreacted AgI and HgI₂ are present in the clusters of the product of interaction. This is as expected since the AgI and HgI₂ clusters before interaction may not be in stoichiometric proposition. This leads to the conclusion that bulk interaction has taken place between microclusters of AgI and HgI₂, the product of interaction being either Ag₂HgI₄ or some complexes between AgI and HgI₂. Thus EDAX, electron diffraction and X-ray diffraction can effectively be used to determine the nature and extent of interaction between clusters of different materials.

6.5 Conclusion

When clusters of two different materials are allowed to interact, bulk interaction may take place between the two. The compound cluster produced by the interaction may consist of a stoichiometric product and some unreacted interactants. Electron diffraction and X-ray diffraction together with EDAX can effectively be used to determine the nature and extent of interaction between clusters of different materials.
References

10.H.Freundlich and F.Moor, Kolloid-Z 36(1925)17.