III. MATERIALS SCIENCE

A. INTRODUCTION

Materials science is a broad field, encompassing a number of areas of chemistry, physics, and engineering, including solid-state physics, inorganic chemistry, and ceramics engineering. An important aspect of this field is the synthesis and characterization of materials which have unusual mechanical, electrical, and thermal properties. This includes broad classes of materials such as sulfides, oxides, glasses, molten salts, polymers, and alloys. Some of these have already been discussed for catalytic applications in Part 1 and, in particular, in Section II of Part 2. To complement these sections, the present section will emphasize three areas: ceramic monolithic substrates as catalyst supports, sintering phenomena, and intermetallic compounds. All three of these areas have found application in catalysis, although the monolith and sintering areas to a much more extensive degree. Brief mention is also made of a few compounds such as novel inorganic polymers which may have potential as catalyst support materials.

The basis for the development of each of these areas, especially as they apply to catalysis, has varied. Monolithic substrates have been developed at a rapid pace over the last five years because of the demand for these structures as catalyst supports for automotive emissions control. Intermetallic compounds, especially those which are very stable at high temperatures have found limited applications in metallurgy, and have not been used extensively in catalysis. However, research over the last decade suggests that these materials may have unusual chemical and thermal stability properties, and therefore numerous potential applications in.

catalysis. Sintering is a phenomenon which has been of interest to materials scientists for a number of years, especially for applications in powder metallurgy. It is of primary concern in catalysis because it leads to crystallite growth, a concomitant decrease in surface area, and therefore a loss in catalytic activity.

This section includes a description of each of these areas, as well as a discussion of possible applications in catalysis. These applications are discussed in further detail in Part 3 for specific processes.

B. MONOLITHIC SUPPORTS

As previously mentioned, the motivation for the development of monolithic catalyst supports evolved from the need for a thermally and chemically durable substrate to support catalysts for automotive emissions control. This has resulted in a commercial technology which is capable of producing materials with a wide range of properties, and therefore which can be considered for other applications in catalysis. In this section, the properties of monolithic materials are described, followed by a discussion of applications.

1. GENERAL PROPERTIES

Monolithic supports are usually composed of small parallel channels of a variety of shapes and diameters. These structures may be in the form of "honeycomb" ceramics extruded in one piece, oxidized aluminum alloys in rigid cellular configurations, or multilayered ceramics formed by corrugation procedures. The channels in honeycomb-like structures commonly have tubular diameters of 1 to 5 mm. The overall diameter of monolithic supports may vary from 1 in. to 2 ft., and is limited, in the case of extrusion processes, by the availability and the operation of the metal die. Materials of fabrication are usually low surface area ceramics such as mullite ($3Al_2O_3 \cdot 2SiO_2$) or cordierite ($2MgO \cdot 5SiO_2 \cdot 2Al_2O_3$). More recently, silicon carbide, silicon nitride, and zirconia have also been fabricated into monoliths. The refractory monolith is produced with macro pores (1-10μ), and may be coated with thin layers (several microns) of catalytic materials, 5-20 wt% coatings being common. The two major advantages of monolithic supports for catalytic operations are high superficial or geometric surface area and low pressure drops during operation. In comparing monoliths with typical packed bed systems, it is not unusual to observe a pressure drop decrease of over one order of magnitude for the same geometric surface area (1). In addition, many of the monolith materials have good thermal conductivity which is an added asset for use as catalyst supports for highly exothermic reactions. A typical comparison of the properties of a monolith versus a packed bed is shown in Table III-1 for the Engelhard HC-Series monolith catalysts (1).

A number of manufacturers produce monolithic substrates in large quantities. This is not surprising since almost 8 million monoliths are used annually in the automotive area. Corning's Celcor is an example of a cordierite honeycomb structure. It is prepared by an extrusion process, and both square and triangular cell shapes are available. Dupont's Torvex is prepared by controlled oxidation of machined aluminum alloys, and is available in alumina or mullite. It is made in three different orientations: a conventional straight cell, a cell slanting at 45^0 from the open cell face, and a crossflow configuration consisting of half cells angled 90^0 to each other and 45^0 to the cell face. American Lava's Thermacomb is a corrugated cordierite ceramic. It is manufactured in two basic structures, honeycomb (no separator between corrugated layers) and split-cell (with separator). From these two basic structures, three additional configurations can be formed, crossflow split cell (alternate cell layers at 90^0),

TABLE III-1

COMPARISON OF PROPERTIES OF HC-CATALYSTS WITH PARTICULATE TYPES (1)

	HC-Series		Particulate Types	
	7 c.p.i.*	4 1/2 c.p.i.*	1/8" particles	1/4" particles
Surface area (m^2/liter)				
Superficial	1.98	1.17	1.11	0.48
Catalytic	4×10^5	4×10^5	1.28×10^5	3.44×10^5
Voids in packed bed (%)	65-70	82	38.5	41.5
Pressure drop/ft. of depth at: Linear velocity = 20 ft./sec. Pressure = 100 p.s.i.g. Temperature = 500°C	0.6 p.s.i.	0.3 p.s.i.	16.5 p.s.i.	10.1 p.s.i.
Ratio of vessel diameters for ΔP = 1 p.s.i. at operating conditions (100,000 space velocity for HC, 60,000 for particles referred to 1.0 for HC-4 1/2 c.p.i. particles)	1.25	1.0	4.0	3.25
Commercially usable space velocities (SCFH/CF)	90,000-140,000	90,000-140,000	20,000-60,000	20,000-60,000
Bed orientation limits	None. Can be mounted horizontally, vertically, etc.		In general, catalyst must be contained in vertical column, with gas downflow.	

* Channels per linear inch.

crisscross split cell, and crisscross honeycomb (alternate cell layers at 45°). Other manufacturers include General Refractories and Davison Division of W. R. Grace. It is clear that the monolithic structures, which were commercialized only a few years ago, are now a well established and readily available commodity.

Cordierite and mullite are the common materials of construction for commercial monoliths with cordierite being more common because of its preferred thermal properties. The mullite structures are more sensitive to thermal shock, but are more stable at higher temperatures. The effects of thermal degradation on the composition of cordierite structures have been studied by x-ray diffraction analysis (2, 3). Up to 2200°F, there is no change in the small mullite concentration which most cordierite contains (15-19%). At 2400°F the mullite concentration increases quite sharply to 24% after 24 hours and to 28% after 72 hours. This precipitation of mullite ($3Al_2O_3 \cdot 2SiO_2$) is brought about by the degradation of the cordierite structure ($2MgO \cdot 5SiO_2 \cdot 2Al_2O_3$) at high temperatures. It is also accompanied by a change in the α-Al_2O_3 concentration which goes through a maximum with temperature (2). The formation of α-Al_2O_3 is probably due to the sintering and crystalization of the γ-Al_2O_3 washcoat. The loss of α-Al_2O_3 at higher temperatures comes about because of the reaction of cordierite with α-Al_2O_3 to form mullite and spinel ($MgO \cdot Al_2O_3$).

$$\underbrace{2MgO \cdot 2Al_2O_3 \cdot 5SiO_2}_{\text{Cordierite}} + \underbrace{15Al_2O_3}_{\alpha\text{-Alumina}} \longrightarrow \underbrace{5(3Al_2O_3 \cdot 2SiO_2)}_{\text{Mullite}} + \underbrace{2(MgO \cdot Al_2O_3)}_{\text{Spinel}}$$

All of these changes involve solid-state reactions, and therefore only occur to any substantial degree at high temperatures (> 2200°F). For most applications in coal conversion where they might find application, this thermal limitation would not be a problem.

2. CATALYTIC APPLICATIONS

The major application of monolith substrates has been as a catalyst support for automotive emissions control (primarily hydrocarbon and CO oxidation). This catalyst is typically 0.3 wt% Pt on a cordierite monolith which contains a 10-15 wt% washcoat of γ-Al_2O_3 (2-11). The primary advantages of these structures over normal packed beds are low pressure drop and minimum attrition rates. This is particularly important for the automotive application where gas flows are typically 100,000-200,000 v/v/hr. and substantial mechanical vibrations are commonplace. These catalysts typically operate at 1300-1600°F, and survive frequent transients up to 2000°F. The catalysts are reported to be effective for 50,000 miles in controlling hydrocarbons and CO within EPA specifications.

Monoliths have also been studied for other reactions. For example, Campbell showed for the Corning extruded structures that a monolithic geometry can be chosen to give higher effectiveness factors(1), and higher rates than a packed bed whenever the effectiveness factor is low for a given catalytic reaction. Two model reactions which he studied were cumene cracking and ethanol dehydration.

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(1) The effectiveness factor is a dimensionless number which is the ratio of the observed reaction rate to that which would be obtained if the whole of the internal surface of the catalyst pellet were available to the reactants at the same concentrations as at the external surface on the pellet. For first-order reactions this ratio is a function of the dimensionless modulus, $d(k/Dr)^{1/2}$ where d is a measure of pellett size, k is the rate constant for unit area, D is the diffusion coefficient of the reactants, and r is the hydraulic radius of the pores. This modulus can also be re-written as $d(k\sigma/D)^{1/2}$, where σ is the catalyst surface area per unit volume.

Other applications for these structures include NOx abatement (1), catalytic combustion for energy generation (13, 14), and emissions control for incinerators (15). For the catalytic conversion of coal, areas where these materials might be considered for application are methanation, Fischer-Tropsch synthesis, and the water-gas shift reaction. However, it should be recognized that the incentive to use these materials may depend significantly on obtaining marked advantages in catalyst life and activity since it is likely that an equivalent volume of packed bed catalyst would be much lower in cost. The application of monolith catalysts to the specific reactions mentioned above are discussed in further detail in Part 3, particularly for methanation.

C. INTERMETALLIC COMPOUNDS

In Part 1 of this study, multimetallic catalysts were discussed in detail. However, there exists another class of materials which, in principle, falls into this same category, but in practice has not been explored extensively in catalysis, namely intermetallic compounds. An intermetallic compound may be defined as an alloy of two or more metals which has a characteristic crystal structure and a definite stoichiometry. This is in contradistinction to homogeneous alloys for which no order may be present. More specifically, a group of binary intermetallic compounds has been studied by materials scientists which exhibits remarkable stability and which shows promise for a number of applications where chemical and thermal stability are important. In these intermetallic compounds the metal-metal bonds are more directed, and in many instances are stronger than those characteristic of substitutional or interstitial alloys. These intermetallic compounds which usually consist of a combination of two metals from opposite ends of the periodic table have been extensively investigated by metallurgists. In this section, the nature of ultrastable intermetallic compounds is discussed, and several examples are given which serve to illustrate this stability. This is followed by a brief discussion of the possible application of these materials in catalysis as well as the problems involved in preparing them in a form amenable for use as catalysts.

1. GENERAL PROPERTIES

Much of the work in this area has been stimulated by the studies of Engel (16-19), Brewer (20-22), and Hume-Rothery (24-27). The work of Engel and Brewer, in particular, has resulted in the development of correlations which predict the structures of alloys and intermetallic compounds. The correlation between electron configuration and metallic structure was first described by Engel (17), and later extended by Brewer to include alloys and intermetallic compounds. Brewer has shown that using this correlation one can predict the composition limits of phases in transition metal alloys, although the generality of this procedure has been disputed by Hume-Rothery (24). The detailed procedures for using the Engel-Brewer correlations have been described elsewhere (20-22). For the present study, a brief description will suffice as it is the physical and chemical properties of intermetallic compounds which are of primary interest.

In using the Engel-Brewer correlation, it is assumed that the crystal structures of the metallic elements are based on definite electronic states of the composite atoms. The unpaired electrons take part in crystal bonding, but the d electrons play no part in determining the type of crystal structure, which is controlled only by the number of s and p electrons. The b.c.c., h.c.p., and f.c.c. structures are regarded as resulting from 1, 2, and 3 (s+p) electrons, respectively. However, the d electrons can have a profound effect on those properties which are related to the electronic configuration changes between the pure elements and the intermetallic compound.

For predicting structure or thermodynamic properties one needs to define the electronic state of the atoms in the pure metals and in the intermetallic compound formed from these metals. This is usually done by choosing the ground state of the free atom or the lowest excited state which avoids the existence of s^2 sub-groups, since the latter is considered as non-bonding. In some instances, this configuration is rejected in favor of one which involves more bonding electrons. For example, for rhenium, the ground state is d^5s^2, and the first excited state is d^6s (excitation energy of 6 kcal/mole) with a second excited state of d^5sp (excitation energy of 46 kcal/mole). Here the d^6s configuration involves 5 bonding electrons because two of the d electrons are paired, and therefore it is rejected in favor of the d^5sp configuration which has seven bonding electrons. Thus, the result is that one predicts that rhenium would form an h.c.p. structure because of the 2 (sp) electrons. In fact, this is the case.

As another example, the ground state configuration of Mg is sp, and this indeed agrees with the observed h.c.p. structure for the metal. Aluminum, which is f.c.c., is satisfactorily explained by the known sp^2 electron configuration.

The Engel-Brewer correlations may be applied to alloys in a similar way. Here, Brewer has determined the tolerance which one might expect on either side of the 1, 2, and 3 (s+p) electrons which correspond to the b.c.c., h.c.p., and f.c.c. structures, respectively. Having determined these limits, the corresponding compositions in a given binary alloy or intermetallic system can be estimated, and therefore the phase diagram determined. This has been done successfully for a number of intermetallic systems (20-22).

The Engel-Brewer correlation also provides a means for calculating thermodynamic properties provided that the electronic configuration of the gaseous elements is known. It was in this way that a group of intermetallic compounds were first predicted (20, 21, 22) and then experimentally shown (21, 28) to have extraordinary thermal and chemical stabilities. These are frequently called Brewer compounds in the literature. Thus, the application of the Engel-Brewer correlations to transition metal alloys predicts that intermetallic compounds of metals of the second and third transition series which are prepared by combining transition metals from the right and left of the periodic table, will have unusual stability. By this model, transition metals of the fourth and fifth periods and Groups I-VII, i.e. Rb to Tc and Cs to Re, use all of their valence electrons for bonding, while Groups VIII-IB, i.e. Ru to Ag and Os to Au do not use all of their valence electrons for bonding in the pure metals. This is because some of the d electrons are paired internally and are unavailable for bonding. As Brewer indicates (21), the difference between the metals from the left and right sides of the periodic table can be summarized in terms of incomplete use of available bonding orbitals and complete use of available electrons on the left side (e.g. Zr), and incomplete use of electrons and full use of bonding orbitals on the right (e.g. Pt). For an intermetallic compound formed from these two classes of metals, an electron transfer occurs from the metal with a surplus of unpaired electrons to the metal with low-lying vacant bonding orbitals to maximize utilization of all electrons and orbitals. This gives rise to unusual thermal and chemical stability.

The formation of $ZrIr_3$ is an example of this stabilization. According to the Engel-Brewer correlation, the electron configuration of

Zr in the h.c.p. structure is d^2sp. The configuration of Ir in the f.c.c. structure is d^6sp^2 with only seven electrons available for bonding since one pair of d electrons is paired internally. In forming $ZrIr_3$, Ir donates electrons to Zr to approach the configuration d^5sp^2, while Zr accepts these electrons to assume the configuration d^4sp^2. If these configurations are attained, the number of electrons used for bonding in the intermetallic compound is increased from 25 for the pure elements to as many as 31 per $ZrIr_3$ entity in the intermetallic compound.

For a given element on the left side of the periodic table, e.g. Zr, the number of electrons transferred, and therefore the increase in the number of bonding electrons is predicted to <u>increase</u> as the other metal is changed from Os to Pt. The stability of the intermetallic compounds should therefore increase in the same direction, i.e.

$$\text{Zr-Pt} > \text{Zr-Ir} > \text{Zr-Os}$$

Brewer therefore predicts that for a given metal on the left, say Zr, the stability of the intermetallic compound should reach a maximum at Group $VIII_3$ (Ni, Pd, Pt). Similarly, for Pt in combination with metals on the left, say Mo, Nb, Zr, stability is predicted to go through a maximum at Group IVB (Ti, Zr, Hf).

In spite of the controversy associated with the broad application of the Engel-Brewer correlations, a significant number of experimental data exist to substantiate the qualitative, and in many cases the quantitative aspects of these correlations. Some of these data are discussed next.

2. SUPPORTING DATA

An indication of the stability of Brewer compounds such as $ZrPt_3$ and $ZrIr_3$ can be seen from the results of experiments in which Pt, Ir, and Os were heated with ZrC (21). In each case, the carbide is decomposed to form graphite and the corresponding intermetallic compound. This shows that these intermetallic compounds have free energies of formation which are more negative than -47 kcal/mole of ZrC, one of the most stable carbides known. The compounds formed were identified as h.c.p. $ZrPt_3$ (ordered $TiNi_3$ structure), $ZrIr_3$ (ordered $AuCu_3$ structure), and h.c.p. solution of Zr in Os.

An even more impressive example is the work reported by Brewer (21) in which a ZrO_2/Pt mixture was reduced in hydrogen, giving $ZrPt_3$ at only 1200°C. In fact, the enthalpies of such reactions are so negative that in some instances explosions have been reported for the adiabatic reaction between the powdered elements (initiated at 1000°C) (29).

Ficalova, et al. (30) prepared $HfPt_3$ and $ZrPt_3$ directly from the elements by electron beam and DC arc melting, and investigated the thermal and chemical stability of films of these compounds. A series of 7000 Å thick films of $ZrPt_3$, $HfPt_3$, and Pt was subjected to 60 sec. pulses of an oxy-propane and an oxy-acetylene flame. The Pt film failed while there was no effect on the intermetallic compounds. Similar work with boiling acids such as aqua regia showed the intermetallics to have superior chemical resistance

Work by Berndt, et al. (31) showed that intermetallic compounds such as Rh_3Th, Rh_3U, Pt_5Th, among others, could be prepared from the respective oxides and the noble metal at exceptionally low temperatures in the presence of hydrogen because of the high thermodynamic driving force provided by the enthalpy of formation for the intermetallic compound. This is remarkable in view of the almost impossible task of reducing ThO_2 or UO_2 with hydrogen to the metal at even the highest attainable temperatures.

Similar results were observed by Darling, et al. (32, 33) for Pt/ZrO_2 and Pt/ThO_2, and confirmed by Erdmann and Keller (34). In the latter study, intermetallic compounds such as Rh_3Th, Rh_3U, Ir_3U, Pd_3Th, Pd_4U, Pt_3U, Pt_3Th, and others were formed in hydrogen from the oxide and noble metal at temperatures as low as 1200°C. Further studies by these workers (35) showed that numerous ultrastable intermetallic compounds could be formed between the Group VIII metals and the rare earths and actinides.

The work which has been done with intermetallic compounds over the last decade clearly shows these materials to have unusual chemical and thermal stability. However, many of the more interesting materials are difficult to prepare in a form which is readily studied in catalysis (i.e. high surface area), and therefore have not been investigated very much for this application. However, there is promise that this problem can be overcome. Examples of the few catalytic studies in this area are discussed next.

3. CATALYTIC APPLICATIONS

As mentioned above, the more stable intermetallic compounds are difficult to prepare, and therefore little catalytic work has been done with these materials. The reason these materials are difficult to prepare is because of the high temperatures necessary to bring about reaction of the refractory oxides involved. For example, in making $ZrPt_3$, one might conceivably impregnate ZrO_2 or an Al_2O_3-supported ZrO_2 with a Pt salt, and reduce in very dry pure hydrogen. Because the thermodynamic driving force to form this compound is extremely high ($\Delta H \gtrsim 100$ kcal/mole), the temperature required to form it is substantially less than that which would be necessary to form other conventional alloys with Group IVB metals. However, it is still a relatively high temperature ($\sim$1100-1200°C) for maintaining surface area for most catalytic materials(1). Thus, ZrO_2 and Al_2O_3 would be expected to sinter to surface areas less than 1 m^2/g. This makes testing of the catalytic properties of such materials a difficult problem. However, as discussed in Part 1, advances in stabilization of supports to very high temperatures (as high as 1200°C) now provide some hope for preparing these so-called Brewer compounds. This could involve the use of thermally treated aluminas, chemically stabilized aluminas, or possibly ultrastable zeolites.

There have been only a couple of catalytic studies with the Brewer compounds. For example, there is some indication that the Russian workers have used certain very stable intermetallic compounds such as $ZrAl_3$ for fuel cell catalysis (36). The catalyst was prepared by electrodeposition, and the data are few and difficult to interpret.

In other work by Ewe, et al. (37), $LiNi_5$ was studied as a fuel cell oxidation catalyst. The results for a hydrogen fuel cell were limited, but encouraging in terms of activity.

The small amount of catalytic work which has been done with the more easily prepared intermetallic compounds has included materials such as Cu_3Au, Cu_2Mg, AgSb, SbSn, Cu_2Sb, WCo_3, among others (38). They have been looked at primarily for simple hydrogenation reactions and formic acid decomposition, and while various electronic theories have been developed to explain the catalytic results and their correlation with the properties of the intermetallic compounds, the results have been relatively unimpressive. This work is reviewed in some detail in reference 38.

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(1) The thermodynamic data are not well defined, therefore this temperature requirement may be a kinetic limitation.

A patent issued to the British Petroleum Company (39) discloses the use of numerous intermetallic compounds such as Pt_3Co, $PtNi_3$, $PtCu_3$, and others for catalytic reforming of naphthas to high octane gasoline. A number of these intermetallic compounds were supported on Al_2O_3, and claimed to be excellent catalysts for the dehydrocyclization reaction (paraffins $\longrightarrow$ aromatics).

The exploitation of intermetallic compounds in catalysis remains to be seen. Advances in catalyst preparation and the need for more thermally and chemically stable catalysts for many new applications are the primary driving force to explore these materials.

4. FUTURE DIRECTIONS

The broad class of intermetallic compounds, especially the very stable Brewer compounds, offer a number of potential applications in catalysis, possibly in the synthetic fuels area. Thus, it may be possible to prepare supported intermetallics, which have unusual thermal and chemical resistance, by combinations of the Group VIII metals with metals like Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W. Because of the very strong interactions involved in forming these compounds, sintering (discussed in the next section) is expected to be significantly reduced. This strong interaction is also expected to modify the electronic and therefore the catalytic properties of the Group VIII, metal. In some instances, this may result in less desirable catalytic properties. For example, in a material like $ZrPt_3$, it might be that such extensive electron withdrawal occurs from the Pt atoms to the Zr atoms, the Pt becomes highly electron deficient, and therefore less metallic than zero-valent platinum. This might diminish the unusual catalytic properties associated with this noble metal. It may be possible to decrease and control this interaction by using elements to the left or right of Zr(e.g. Mo) as the second element.

The metal-metal interaction in intermetallic compounds can also be looked at in another way. Thus, in following the arguments presented by Dalla Betta and Boudart (40) for Pt-loaded zeolites, the electron transfer which occurs in forming the intermetallic compound can also be used to control various properties. For example, in the case of the Pt zeolite, atomic clusters of Pt were found to donate electrons to the zeolite structure, making the Pt behave catalytically like Ir. Donation of electrons in the intermetallic compounds may directionally produce the same effect.

Another parameter which this electron transfer may affect is tolerance to electrophilic poisons such as sulfur, nitrogen, arsenic, and phosphorous. These elements tend to poison metals like Pt by adsorbing strongly on their surface with strong electron withdrawal. If the interaction between Pt, Pd, or any other metal on the right side of the periodic table with one on the left is strong and follows Brewer's prediction of electron transfer, then one would expect the interaction of these catalytic metals with electrophilic poisons such as those mentioned above to be substantially reduced.

A significant amount of research is necessary before the catalytic properties of the Brewer type intermetallic compounds can be assessed. As mentioned above, a primary difficulty in studying these materials has been preparation in a form which can be readily studied in catalysis. The advances which have been made in catalyst preparation over the last decade (see Part 1, Section V) should contribute to solving some of these problems. Intermetallic systems may find applications in upgrading coal liquids, methanation, water-gas shift catalysis, and Fischer-Tropsch synthesis. However, much research would have to be done before there could be any indication of success in these applications.

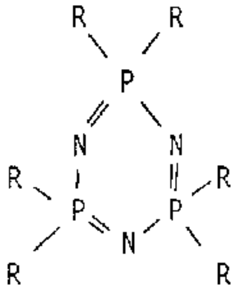
D. MISCELLANEOUS MATERIALS

There are a couple of other classes of materials which have not been discussed in prior sections, and may offer some possibilities for applications in catalysis. The first of these involves the development of technology to "spin" refractory oxides into high surface area fibers. For example, Imperial Chemical Industries, Ltd. offers their Saffil Al_2O_3 and ZrO_2 fibers with surface areas varying from 1.5 to 160 m^2/g for the Al_2O_3 and 7.5 to 10 m^2/g for ZrO_2 (41). The Al_2O_3 fibers are reported by ICI to withstand temperatures in excess of 2750°F depending upon use, while the ZrO_2 material can operate at 2900°F. The fibers can be fabricated into numerous forms including monolithic structures, thimbles, cylindrical filters, and cloths. Because of the thermal stability, high surface area, and the fabrication properties of these materials, they represent a possible new class of catalyst supports. Potential applications include many of those for which monolithic supports are used. Only minimal catalytic work has been reported as yet for these materials in the literature (41), and therefore it will be some time before an evaluation can be made of their real potential.

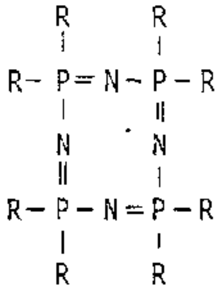
A second broad class of materials has recently been developed because of work at the interface of inorganic chemistry and polymer science. Examples are the new inorganic polymers of nitrogen with phosphorous (42, 43) and nitrogen with sulfur (44). Not enough work has been done with the sulfur-nitrogen polymers to speculate as to whether these materials might have an application in catalysis. The phosphorous-nitrogen polymers, on the other hand, exhibit interesting properties which are worth noting for this purpose.

The nitrogen-phosphorous polymers, called poly-organophosphazenes, have recently aroused considerable technological interest because of numerous possible applications ranging from high-temperature lubricants and polymers to new synthetic rubbers.

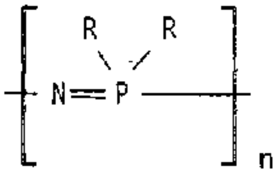
They are made from phosphazene linkages which are cyclic or linear molecules containing alternate phosphorus and nitrogen atoms in the skeleton, with two substituent groups attached to each phosphorus (42), e.g.



(a)



(b)



(c)

The cyclic trimer and tetrameric chlorophosphazenes have been known for many years. They are synthesized by elimination of HCl from the reaction between NH_4Cl and PCl_5 at about 120°C. They are readily converted, by heating, to a transparent elastomeric polymer, called "inorganic rubber" (42). It has unusual properties because its elastomeric characteristics persist from -50°C to +350°C. It swells in organic solvents, but does not dissolve. It also has remarkable resistance to thermal degradation. Indeed, it would be a valuable technological material were it not for the fact that it slowly reacts with moisture in the atmosphere and hydrolyzes to H_3PO_4, HCl, and NH_3. This hydrolytic decomposition is brought about by reaction of moisture with the chlorine groups and not by scission of nitrogen phosphorus bonds. To solve this problem, recent studies have been directed at changing the chlorine to other groups (43, 44). This work is making significant progress, and it is now possible to synthesize a number of these polymeric materials with high thermal and chemical stability.

Possible applications of these polymers in catalysis are primarily as support materials. They offer several properties of interest, including mechanical durability, thermal and chemical stability (especially compared to organic polymers), and the possibility of adding catalytic functions by attaching various groups to the polymer, including organometallics. However, it should be pointed out that a significant amount of work may be necessary to assess the value of these materials in catalysis.

E. SINTERING

Sintering is the coalescence of small particles or atoms at elevated temperatures caused by diffusion of species with a resultant loss in surface area. The motivation for materials scientists to study this phenomenon is provided by a number of practical applications. For example, the techniques used in powder metallurgy depend heavily on an understanding of this subject. The rate of migration and coalescence of internal voids in metals, as they are for example, generated in nuclear reactors, is governed by surface diffusion processes (45). The process of crystal growth from the vapor phase has been recognized to depend on surface diffusion of adatoms (46). The technology of the film semiconductor devices is in many ways related to the process of surface diffusion, e.g. through nucleation and growth of epitaxial films (47).

More recently, scientists and engineers in catalysis research have begun to apply the principles developed in materials science concerning sintering to problems involving catalyst deactivation (48-54). The primary objective of this work has been to understand those processes which lead to a loss in catalyst surface area, and therefore catalytic activity. It is this aspect of sintering which is treated in this section.

1. THEORETICAL ASPECTS

Although sintering refers to those processes which result in surface area loss for solids in general, most of the work of catalytic interest has been done for metals, and in particular for supported metal catalysts. There have been several theoretical treatments of the processes involved.

For example, Ruckenstein and Pulvermacher (55, 56) developed a model which depicts sintering of metals as occurring via migration, collision, and fusion of metal crystallites on the support surface. In this treatment, either migration or coalescence can be rate-determining with the rate of change of the metal surface area S being described by an equation of the form

$$dS/_{dt} = -KS^n \qquad \text{(III-1)}$$

where K is a constant and n can vary from 2 to 8 depending upon the way in which the rate-determining step is assumed to depend upon metal particle size. These authors have applied their model to several experimental studies, and showed examples of both diffusion limitations (n=2 or 3) and coalescence limitation ($4 \leq n \leq 8$).

The scheme developed by Flynn and Wanke (54, 57) treats the sintering process as a two-dimensional evaporation-condensation process. An equilibrium is assumed to be reached between metal atoms on the metal catalyst particles and those which have migrated to the support surface. The rate at which atoms dissociate from metal particles is assumed to be independent of particle size, while the rate of atom recapture is taken to be proportional to particle diameter. Therefore, larger particles grow at the expense of smaller ones. In this respect, it should be noted that the concentration of metal atoms in equilibrium with small particles is greater than that around larger particles. This phenomenon is expressed analytically by the Kelvin equation. The difference in concentration leads to a transport of metal atoms from smaller to larger particles. This phenomenon is also well known for the case of solid particles in a liquid phase, and is known as Ostwald Ripening. The Flynn-Wanke model suggests that the size of metal particles or more precisely the distribution of particle sizes determines the value of the exponent as in equation III-1. It is therefore obvious that n will vary during the course of any sintering process.

Finally, there is a model which has been proposed by Wynblatt and Gjostein which considers in some detail the various processes involved in sintering supported metal catalysts including crystal nucleation and growth, particle migration and coalescence, and surface or vapor transport of the metal. These authors calculate order of magnitude rates for these various steps using data obtained primarily for pure metals or supported metal films rather than supported metal catalysts. They conclude that particle growth can occur in either a "non-inhibited" or "inhibited" mode. As Schlatter (48) points out, the Ruckenstein-Pulvermacher model (migration, collision, and coalescence) and the Flynn-Wanke model (dissociation, diffusion, and recapture) are examples of non-inhibited particle growth. Wynblatt and Gjostein's idea of inhibited growth stems from their observation that platinum particles on a flat alumina surface approach a limiting size. They attribute this to faceting of the metal crystallites. Therefore, crystallite growth is suggested to be inhibited by the requirement of a nucleation process for each new layer of atoms added to a particle.

There are a number of differences among these three models. For example, the Ruckenstein-Pulvermacher model assumes transport by particle migration whereas the Flynn-Wanke model makes use of atomic diffusion. Ruckenstein and Pulvermacher argue that the interaction between metal atoms and common catalyst support surfaces would be too weak to make dissociation energetically favorable as suggested by Flynn and Wanke. They also mention that the rates of atom evaporation would be too low to account for observed sintering rates. It should be mentioned that according to the Flynn-Wanke and Wynblatt-Gjostein models the diffusion can take place as a two-dimensional gas on the surface or three-dimensional, i.e. into the gas phase with re-adsorption on the surface of the support. This is particularly true in the presence of reactive gases such as oxygen, carbon monoxide, or halogens. For example, nickel is readily transported both on the surface and in the gas-phase as nickel carbonyl in the presence of CO. Similarly, platinum is transported as PtO_2 in the presence of oxygen. Reactive gases can, however, promote sintering only at conditions where the bulk metals are stable. Neither the metal compound formed nor the surface compound with the support can be more stable than the bulk metal, otherwise increased dispersion of the particles will result. This latter aspect will be discussed later.

Wynblatt and Gjostein agree that gas phase or surface migration of metal atoms is ruled out in a reducing environment, however, they suggest, as mentioned above, that in an oxidizing environment some metals (e.g. Pt) can migrate as oxides (e.g. PtO_2). The differences between these models point to the need for additional data to clarify the nature of the sintering process and to provide ideas for model development and refinement.

Although there are differences among these three models, they do agree on some general aspects. For example, all three models predict that large metal crystallites will grow at the expense of small ones at elevated temperatures. This is observed experimentally. One might also deduce that the pore structure of the support would tend to stabilize the metal dispersion, as would increased metal-support interactions. These effects are also observed experimentally, and have been discussed in some detail in Part 1. Also, as observed by Schlatter (48), all three models can account for the fact that platinum sinters more readily in an oxidizing environment than in a reducing environment. However, this appears to be an after-the-fact correlation with experiments. Indeed, there is a real need for more controlled experimental kinetic data to develop more exact theories of the sintering process. Some of the available experimental data are given in the next section.

2. EXPERIMENTAL DATA

As mentioned above, the amount of useful sintering data which are directly applicable to catalysts are few. However, there are some pertinent studies which have stimulated the development of the models discussed in the previous section.

A general observation which is well documented is that supported metal catalysts are thermally more stable than unsupported metal catalysts. Thus, while unsupported platinum sinters severely under even the most mild conditions (58-60), this same metal dispersed on refractory oxide supports such as Al_2O_3 is stable at reasonably high temperatures ($\sim 800^\circ C$) (61).

The sintering rate depends markedly on temperature, time, and gaseous environment. Herrmann, et al. (62) found that the sintering rate for platinum supported on γ-Al_2O_3 increased with increasing temperature and time in nitrogen, and was second order in the platinum area remaining. Maat and Moscow confirmed this second order behavior for a platinum on γ-Al_2O_3. However, Kirklin and Whyte (63) found that platinum on alumina catalysts do not follow this second order dependence when the sintering is carried out in a hydrogen environment. This suggests a different mechanism for the two environments. Somorjai, et al. (64) reached this same conclusion by studying the sintering of platinum on η-Al_2O_3 in both reducing and oxidizing atmospheres. The sintering rate was found to be faster under oxidizing conditions than under reducing conditions (64-66). The activation energy in a reducing environment was determined to be substantially lower (14-27 kcal/mole) than in an oxidizing environment (44-55 kcal/mole).

An intriguing sintering experiment which indicates that the sintering process may be subject to a number of parameters including rate of cooling was reported by Emelianova and Hassan (60). They found that rapid cooling of a platinum catalyst from high temperatures maintained a high metal surface area. In contrast, slow cooling resulted in a substantial amount of sintering. In view of the above models, one might speculate that slow cooling permits the metal particles which are mobile at these high temperatures to coalesce, and therefore to lose surface area. On the other hand, rapid cooling "freezes" the mobile and highly dispersed transport species present at high temperatures.

Although much of the sintering studies on supported metal catalysts have involved platinum, there is some work which has been done with rhodium (53), palladium (67, 68), and nickel (67, 68). For the palladium work, the metal was supported on silica-alumina (67). High temperatures in oxygen caused the Pd particle size to increase while a hydrogen environment brought about only an annealing of the lattice defects with a resultant decrease in specific catalytic activity, but not surface area. It was also found that certain high valent cations (e.g. Th^{+4}, La^{+3}) which were added to the support enhanced the thermal stability. It could be that these cations hindered surface Pd mobility by increased metal-support interactions (see Part 1).

In other work with palladium, Schlatter (48) reported some interesting experiments where he studied the sintering of Pd on Al_2O_3 in H_2 and O_2 environments and found different results than those reported above for $SiO_2 \cdot Al_2O_3$. After four hours at 650°C in O_2, he observed no decrease in surface area. However, the same treatment in hydrogen decreased the surface area by almost 75%. Even more interesting, an O_2 treatment at 650°C of the sintered sample restored the Pd area. It would appear that the O_2 provides a medium for forming surface PdO species which redisperse the metal on the Al_2O_3 support. This result emphasizes the complexity of the sintering process and its dependence on the type of system that is being considered. Indeed, to completely describe the sintering process, one must consider at least the following variables:

- Structure and stability of the metal surface
- Equilibrium shape or configuration of the metal particles
- Stability of metal particles with respect to dissociation as a function of particle size and shape
- Mobility of metal atoms over the metal surface; note effects of structure on mobility
- Interaction of metal particles and individual atoms from these particles with the support surface
- Mobility of metal particles and atoms over the support surface
- Support Morphology

3. FUTURE DIRECTIONS

Much more extensive experimental work is necessary before the relative merits of the various theoretical models can be evaluated. Studies are needed which concentrate on the metal particle distribution as a function of time, temperature, and gaseous environment. New improved electron microscopic techniques, especially those which record events as a function of time, will be very useful for studying the mechanism of sintering. As an example, the technique pioneered by Baker (69) for studying catalysts in situ during reaction and recording all data on movie film has promise for such studies. Future work should also look at all of the Group VIII and IB metals to develop the systematics of these metals and to highlight the differences and similarities. This will help in the development of more broadly applicable models.

Finally, an area which has not been extensively studied, but is of substantial technological value, is the development of techniques for the redispersion of sintered metals. This involves studies of sintering and redispersion in various reactive environments. The one system which has been studied in much detail is Pt on Al_2O_3 which has been used as a catalyst for the reforming of naphthas to high octane gasoline. It was found some time ago that certain mixtures of halogens, such as chlorine, with oxygen could be used to redisperse agglomerated platinum (70). However, with the rapid growth of multimetallic systems, similar techniques need to be developed for other metals and combinations of metals. This would be very valuable for the regeneration of supported metal catalysts. In terms of catalysis, and in particular the relevance of this area to the catalytic conversion of coal, those processes for which these studies are likely to be important are those where Group VIII and IB metals or combinations thereof will be used and regeneration would be economically rewarding. In addition to certain upgrading processes which are discussed in Part 3, Fischer-Tropsch synthesis, water-gas shift catalysis, and methanation are possible areas of interest.

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