

V. CATALYST PREPARATION

A. INTRODUCTION

For many years catalyst preparation has been regarded as an art, with most of the available information contained in the patent literature and a few review articles (1-5). However, in recent years, there has been an increased effort to put this activity on a scientific basis. This is emphasized by the first international conference which was recently held on this subject (6). Many new techniques have been developed for catalyst characterization, and these have played an important role in understanding the effects of preparative variables on catalytic properties.

This increased insight into the nature of catalyst preparation has led to the synthesis of a number of new catalysts with improved activity, selectivity, and stability properties. Many of these improvements may well find application for the various catalytic steps which are involved in the catalytic conversion of coal. However, to review all of the details of the numerous new concepts in catalyst preparation would be a monumental task in itself, and beyond the scope of the present study. Instead, most of the important techniques which have been discovered or developed over the last decade will be briefly mentioned with adequate references. Those techniques which have obvious or potential application will be discussed in some detail. Emphasis will be placed on the application of particular procedures to the catalytic steps involved in the conversion of coal to clean-burning liquid or gaseous fuels. The reactions of interest have already been described in Section I.

A summary of the primary concepts of interest with some examples, as well as the significance of these concepts and areas for possible application are presented in Table V-1. The table gives a listing of over thirty preparative techniques which for convenience have been divided into six categories:

- Dispersed Materials
- Supported Catalysts
- Controlled Physical Property Supports
- Stabilized Supports
- Stabilized Supported Metals
- Multimetallic Catalysts

It is useful to recognize that many of these preparative procedures can be used commercially. Some, in particular a few of those concerned with the preparation of dispersed materials, may only be practical on a laboratory scale. However, these procedures are still valuable because they make possible the preparation of many new compounds with high surface area, and thereby expedite catalytic testing of readily characterized materials.

This section on catalyst preparation is divided into three parts, metallic catalysts, non-metallic catalysts, and the final part which is a summary of practical implications.

B. METALLIC CATALYSTS

As mentioned in Section II, metallic catalysts have played a major role in the development of petroleum and petrochemical processes. They are also expected to be important for certain aspects of the catalytic conversion of coal. For convenience, the discussion here on the

TABLE V-1

CONCEPTS IN CATALYST PREPARATION

PREPARATIVE OBJECTIVE	TECHNIQUE/MATERIAL	EXAMPLES	REFERENCES	SIGNIFICANCE	AREAS OF APPLICATIONS
Dispersed Materials	Chem. Reduction Flame Decomp. Flame Spraying Support Solub. Impreg. Synth. Ketenide Decomp. Freeze Drying	PtAu ₃ (100 Å) ZrO ₂ , Fe ₂ O ₃ (100 Å) Raney Ni (100 m ² /g) Pt (15 Å) Mg ₂ Mo ₃ O ₈ (100 m ² /g) Ag Clusters W ₂ C (200 Å)	7-11 12 19 13 74 78 14-18	Preparation of high surface area unsupported metals, alloys, oxides, mixed oxides, and complex inorganic materials allows catalytic evaluation of well characterized novel materials.	Fundamental catalytic studies of novel materials Broad Applications
Supported Catalysts	Incip. Impreg. Immis. Liq. Displ. Surf. Impreg. Adsorption Anchoring	Supp. Metals Pt/Al ₂ O ₃ Ni/Al ₂ O ₃ Pt(NH ₃) ₄ Cl ₂ /Al ₂ O ₃ Rh(acac)(CO)-SiO ₂	53,54 59 58 60,61 30	Variable dispersion of active phase gives control of catalytic properties. Anchored complexes obviate separation problems.	CO/H ₂ Synthesis Water-Gas Shift Refining & Upgrading
Controlled Physical Property Supports	SoI-Gels Gel Precip. Homo. pH Change Aerogels Pyrogels	TiO ₂ -SiO ₂ ZrO ₂ -TiO ₂ Ni/SiO ₂ (13 Å) Ni/Al ₂ O ₃ BaTiO ₃	23-25 23-26 62,63 27-29 23	Supports with controlled areas, acidity, pore sizes, and mechanical properties can be made. Homogeneous pH control gives high dispersion of supported metals which are difficult to disperse (e.g. Ni, Co, Fe).	Direct Liquefaction CO/H ₂ Synthesis Water-Gas Shift

TABLE V-1 (cont.)

CONCEPTS IN CATALYST PREPARATION

PREPARATIVE OBJECTIVE	TECHNIQUE/MATERIAL	EXAMPLES	REFERENCES	SIGNIFICANCE	AREAS OF APPLICATIONS
Stabilized Supports	Doping Stab. Zeolites Monoliths Refractories	Al ₂ O ₃ w/Cs ₂ O, La ₂ O ₅ DECAT. Y-Type Cordierite Si ₃ N ₄ , SiC, ZrO ₂	31,32 33-44 49-52 45-48	Supports are available which can endure 1000-1500°C. Ultrastable zeolites and Al ₂ O ₃ are readily prepared. Monoliths open new dimension for catalysts in terms of heat/mass transfer, mechanical properties, pressure drop, and other engineering variables.	Direct Liquefaction CO/H ₂ Synthesis (Methanation) Refining & Upgrading
Stabilized Supported Metals	Metal/Supp. Eff. Bimetallics Trimetallics Sulfidation	Ru/MgO, Ru/BaO PtCo Ru-Ni-Cu H ₂ S-Pt/Monolith	69,70 55,56,68 71 73	Metal catalysts which can endure up to 1000°C can be prepared. They exhibit good activity maintenance after oxidative regeneration.	CO/H ₂ Synthesis (Methanation) Refining & Upgrading
Multimetallic Catalysts	Clusters Supp. Alloys Raney Alloys Organomet. Clusts.	RuCu/SiO ₂ PdAu/SiO ₂ CoNi, NiCu RhCo ₂ /SiO ₂	55,56 57,68 20-22 65,66	Control of catalyst activity, selectivity, maintenance, stability, and possibly poisoning.	CO/H ₂ Synthesis Refining & Upgrading

preparation of metal catalysts is divided into two parts, one on unsupported metal systems and the other on supported systems.

1. UNSUPPORTED METAL CATALYSTS

There are a number of procedures for preparing unsupported metals. However, few of these systems have potential as practical catalysts for the reactions of interest in this study. The details of these procedures have been discussed in a recent review (5). One common technique is chemical reduction of aqueous (7) or non-aqueous (8) solutions containing the metal to be formed. Chemical reducing agents include sodium borohydride (7, 8), hydrazine (9), formaldehyde (10), or hypophosphorous acid (10). High surface area alloys can also be prepared by this procedure (11).

Highly dispersed metals and alloys may also be prepared by flame decomposition (12), i.e. by directing a vapor of a metal salt, such as a metal chloride, into the flame of an oxygen-hydrogen burner, followed by hydrogen reduction of the product to convert the oxide to the metal. Alternate procedures include solubilization of the support in a supported metal catalyst using HF or HBF₄ (13), and freeze drying of an aqueous metal salt solution with subsequent hydrogen or chemical reduction of the finely dispersed salts (14-18).

Two techniques which have been used commercially to prepare unsupported metal catalysts are flame spraying (19) and the preparation of Raney metal alloys (20, 21). The former has been used extensively by the Bureau of Mine Workers (19) to coat heat-exchanger tubes with nickel catalysts for use as a methanation reactor. Direct contact of the catalyst with the exchanger tubes gives high heat transfer rates which is reportedly helpful in minimizing catalyst deactivation during the very exothermic methanation reaction. Raney nickel has

been known for some time (22), however, Raney alloys have only recently been studied. They present the opportunity to use the concepts of bimetallic catalysis (Section II) to modify known unsupported systems such as Raney nickel. The objective of this work would be to improve catalytic properties, especially poison tolerance and resistance to thermal degradation.

2. SUPPORTED METAL CATALYSTS

Although the metal and support in a supported catalyst can interact strongly in some cases (Section III), these constituents generally fulfill markedly different functions. It is therefore convenient to divide the present treatment into a separate discussion of the support and metal phases, respectively.

a. The Support

The techniques for preparing catalyst supports which may have application to the catalytic conversion of coal fall in two general areas, techniques for controlling physical properties and those which increase thermal stability.

The preparation of support materials with controlled surface area, pore volume, and pore size distribution has been the subject of much research over the past several years. The primary motivation for this work has been the development of stable, controlled-pore supports for use in hydrofining residua. Conventional HDS/HDN catalysts have been found to be ineffective, primarily because of the preponderance of small pores. The latter are easily plugged, which effect leads to catalyst deactivation. Research in preparing novel supports has included a number of precipitation and gelation procedures which are broadly applicable to oxide or mixed oxide systems. In the sol-gel process (23) a colloidal sol of metallic oxides or hydroxides is converted to a

semi-rigid gel by a number of mechanisms including removal of water, neutralization with base or removal of acid by solvent extraction. The gel is then dried and calcined to the oxide. The final surface area, pore size distribution, and structure are determined during the gelation stage. In recent years, considerable effort has been devoted by researchers in the nuclear field to exploring the potential of sol-gel technology for preparing metal oxides (24, 25) for subsequent use in fuel rods or other nuclear materials. As a result of this work, it is now possible to prepare a broad range of oxides or mixed oxides with well-controlled physical properties. Materials include Al_2O_3 , TiO_2 , ZrO_2 , Cr_2O_3 , Fe_2O_3 , rare-earths, and mixtures thereof.

Gel precipitation (23, 26) is an alternate procedure also used to prepare oxides or mixed oxides with variable physical parameters. In this technique an organic gelling agent is added to the aqueous metal salt solution before precipitation. On contact with an alkali precipitant (NH_4OH) a co-precipitate is formed in which the metallic hydroxide is held rigidly within the framework of the organic gel. By controlling various experimental parameters in the processes, one can alter the physical properties of the oxide or mixed oxide support material.

One of the more interesting preparative procedures to be developed recently is the Aerogel technique described by Teichner and co-workers (27-29). The mixed nickel oxide-alumina system is a typical example. In this case a mixed aerogel is prepared by adding a small amount of water to a methanol-butanol solution containing dissolved aluminum and nickel compounds (e.g. aluminum sec-butyrate and nickel acetate). The solvent is then stripped in an autoclave under supercritical

conditions, to avoid collapse of the solid texture. If the autoclave is then flushed at high temperatures with hydrogen instead of an inert gas, metallic nickel on an alumina aerogel is obtained. If inert gas is used, a mixed oxide aerogel is the product. By adjusting parameters, one can obtain substantial variations in surface area and pore volume. For example, nickel oxide can be made with a surface area range of 500-800 m²/g (27). Similarly, NiO·Al₂O₃ (160-650 m²/g), MoO₂ (90-287 m²/g), NiO·MoO₂ (210-483 m²/g), and many other combinations are possible. The general procedure has two primary advantages: it produces materials which need little, if any, purification (uses no Cl⁻, NO₃⁻, or Na⁺) and it is extremely quick (~ 2 hrs. to prepare a few hundred grams in a typical autoclave). The mixed oxides prepared this way have also been found to have interesting catalytic properties (27).

The use of gel procedures also permits the preparation of mixed oxides with controlled surface acidity. This is done primarily by controlling the bulk, and therefore the surface composition of the mixed oxides. Acidity control is a major factor for many reactions involving the conversion of coal. As has been reviewed recently (30), it can determine product distribution, overall activity, and activity maintenance. For this reason, preparative procedures which allow control of this variable are important to synthetic fuels technology.

The other broad category concerning techniques for preparing support materials involves those which give increased thermal stability. This factor is particularly important for catalysts which are subject to hot spotting (e.g. methanation) or may require oxidative regeneration (e.g. direct liquefaction).

One procedure for imparting thermal stability to support materials is cationic doping. For example, alumina can be stabilized with respect to high temperature conversion to its α -form. The latter transformation usually decreases surface area from about 250 m²/g to less than 1 m²/g. If alumina is doped with small amounts of oxides from Group IIA (e.g. CaO, SrO, BaO) (31) or the rare earths (e.g. CeO₂, La₂O₃) (32) among others, and subsequently calcined at 1200°C for 2 hours, a stable surface area of 20-100 m²/g is obtained. This can then be used as a thermally stabilized support material. These materials have found application for high temperature reactions such as those encountered in automotive exhaust catalysts and catalytic combustion (see Section III).

The development of zeolites as catalysts and support materials has been an important chapter in heterogeneous catalysis, especially for applications to numerous petroleum and petrochemical processes. They are important because of the broad range of properties possible with these materials. They can be synthesized in a variety of compositions and readily undergo ion exchange with catalytic metals (e.g. Pt, Pd, Ni). Most of these properties and their implications have been reviewed elsewhere (30). Over the last five years, a new class of zeolites has been developed which have remarkable thermal and chemical stability (33-39). These materials survive high temperature hydrothermal conditions and in some cases can be treated at temperatures above 1000°C with no structural collapse. The remarkable thermal stability and broad range of physical and catalytic properties exhibited by these materials makes them attractive for a number of the reactions involved in the conversion of coal. With the exception of direct gasification,

they could find application in all areas, especially upgrading and direct liquefaction. Two particularly interesting applications for these stabilized zeolites are hydrodesulfurization and hydrodenitrogenation. Such catalysts have recently been described in the patent literature (40-44). These catalysts are prepared by a coprecipitation of the molecular sieve-containing hydrogel composite in an aqueous solution containing a number of other catalytic or promoter metal salts. This cogel procedure is similar to the gel preparative techniques previously described in this section. It is in contrast to much of the prior art which describes preparations by coprecipitating only two metal compounds together with a molecular sieve, dehydrating the resulting coprecipitate, and thereafter adding a third or fourth metal component onto the coprecipitate by conventional techniques such as impregnation. The cogel procedure reportedly gives catalysts with unprecedented activity and activity maintenance for HDS and HDN of heavy feedstocks. In one case (41), the catalyst was treated at 1200°C for two hours with no change in surface area (350 m²/g). This stability is ascribed to the increased degree of structural homogeneity which this technique offers. It has been used to prepare NiO·WO₃ (41), NiO·WO₃·ZrO₂ (43), and NiO·WO₃·TiO₂ (42-43) catalysts, all stabilized with ultrastable zeolites.

In the refractories area, some efforts have been applied to preparing silicon carbide (45), silicon nitride (46), and other high temperature compounds in forms which would make them attractive as catalyst supports. So far, the value of these materials over other more readily available supports is not apparent. However, some of the properties may be useful. Silicon carbide, for example,

offers the advantage of high thermal conductivity. This could be of value for highly exothermic reactions, especially where hot spots are likely to occur. Other materials such as aluminum borate (5-100 m²/g, stable at 1300°C) (47) and boron phosphate (200 m²/g, stable at 500°C) (48) have also been developed and may find use in the coal conversion area.

Finally, in the support area, it is worth noting the development of monolith support structures (49-52). Monolithic supports were developed primarily for automotive catalysis and are 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 ceramic corrugations. The channels in honeycomb-like structures have tubular diameters of 1 to 3 mm. Materials of fabrication are usually low surface area ceramics such as mullite (3Al₂O₃·2SiO₂) or cordierite (2MgO·5SiO₂·2Al₂O₃). More recently silicon carbide, silicon nitride, and zirconia have also been fabricated into monoliths. The refractory monolith is produced with macropores (1-10μ), and may be coated with thin layers of catalytic materials, 5-20 wt.% coatings being common. The two major advantages of monolithic supports for catalyst operations are high geometric surface area and low pressure drop during operation. In comparing monoliths with packed beds, it is not unusual to observe a pressure drop decrease of over one order of magnitude for the same geometric surface area. These advantages combined with the increased thermal conductivity of these materials make the monolith structures possible candidates for highly exothermic reactions (e.g. methanation).

It is apparent that some of the above preparative techniques may have potential for synthesizing support materials for a number of areas in the catalytic conversion of coal. Some of these will be summarized in Section V.D.

b. The Metal

In the preparation of a supported metal catalyst, two factors are usually of primary importance; maximizing metal dispersion by using the appropriate preparative procedure, and maintaining dispersion during reaction. The first factor, in general, assures maximum catalytic activity. The second, as discussed in Section II, is related to activity maintenance. Crystallite size and metal-support interactions can become noticeably significant at high dispersions. These will not be emphasized here, but are treated in detail in Section III.

A number of techniques have been developed to maximize dispersion of the metal on a support. The proper choice of procedure depends upon the chemistry involved for a given procedure, and the compatibility of this chemistry with the surface properties of the support. The most common technique involves impregnation of the support with an aqueous solution containing salts of the catalytic metals. This is usually accomplished by incipient wetness (53), i.e. using only enough solution to just fill the pores of the support. Sometimes the catalyst is evacuated prior to impregnation to insure homogeneous distribution of the solution throughout the catalyst pellet (54). The impregnation technique has been successfully used to prepare bimetallic cluster (55-56) and alloy (57) catalysts. It can also be used in modified form to surface impregnate pellets (58). This is accomplished by first impregnating the catalyst pellets with an organic liquid such

as toluene to such an extent that only a thin surface element of the pellet is left dry. This is then impregnated with an aqueous solution of the metal salts to give a surface coated pellet. The pellets are subsequently dried, driving off the organic and the water. This form of catalyst is useful for reactions which are run under mass transfer limitations or where excessively high temperatures are likely to be generated in a pellet center. In theory, these effects can be alleviated by using smaller diameter pellets, however, for some reactors this leads to an excessive pressure drop and radial temperature gradients.

An interesting systemization of incipient wetness impregnation has been recently proposed which provides a greater degree of control of the parameters involved in the preparative process. This technique is called the Displacement of Immiscible Liquid (DOIL) impregnation procedure (59). It involves slurring the support with a water-immiscible liquid in a high-speed mixer and adding the aqueous impregnating solution. Because most common oxide supports such as alumina or silica are more hydrophylic than oleophylic, the aqueous solution displaces the water-immiscible liquid from the pores of the support, and the latter is thereby impregnated. Preparative parameters are easily controlled for reproducibility. It is surprising that this procedure has not received greater use.

Supported metal catalysts are also prepared in high dispersion by adsorption techniques (60-61). These involve either cationic (61) or anionic (60, 61) adsorption of the metal species from solution to the surface of the support. The crucial aspects of the support-surface chemistry and how it interacts with the solvent medium have only recently been recognized (60). This is likely to lead to novel

procedures for catalyst preparation by impregnation and adsorption.

A technique which has potential applications for a number of areas in the catalytic conversion of coal because it leads to relatively stable and highly dispersed supported metal catalysts is the homogeneous pH-change procedure developed by the Dutch workers (62-64). In this method, the precipitant (hydroxyl ions) is generated homogeneously throughout a suspension of the support in a solution of the active metal by thermal or chemically-assisted decomposition of urea. The homogeneous generation of hydroxyl ions prevents local concentration gradients, and therefore gives a homogeneous precipitate with higher surface area. If the precipitating compound nucleates more easily at the surface of the carrier than in pure solution, a precipitation onto the support is obtained. Using this procedure, the Dutch workers have prepared nickel catalysts on silica at the 13-70 wt.% level with corresponding crystallite sizes of 15-40 Å (63, 64). This is equivalent to nickel surface areas in the range of 170-450 m²/g Ni. The technique has broad application, and should also find use in synthesizing multimetallic systems.

A few other techniques for obtaining high dispersion can be mentioned. The aerogel procedure (27-29) has previously been described in Section V.B.1.a. as a technique for preparing highly dispersed supported metals as well as support materials. The use of organometallic precursors is another procedure which has recently been studied. This technique is of particular value in preparing structurally well-defined multimetallic systems (65, 66). This approach makes use of transition metal complexes which exhibit bonding between atoms of the different metals involved. In a specific example (65), a supported cobalt-rhodium catalyst was prepared by impregnating silica with a hexane

solution of $[\text{Co}_2\text{Rh}](\text{CO})_{12}$. The supported complex was then decomposed and reduced to the metals. A strong interaction between the metals was evident because the catalytic properties observed for the bimetallic system were significantly different from those of the pure metals (65). This preparative procedure has value in exploring the utility of model multimetallic systems in a number of areas (e.g. CO/H_2 synthesis reactions).

In the organometallic area, one also has to consider the use of such complexes both in the homogeneous phase and "anchored" to supports. These will be reviewed in some detail in Part 2 of this study, in the discussion of other disciplines which may impact on catalytic coal conversion. However, it can be noted here that these catalysts and preparative procedures are likely to find greatest application in the CO/H_2 synthesis area. As will be discussed later, they present the possibility of more selective reactions at milder conditions, and as recently reported (67), possibly even increased resistance to poisons such as sulfur. However, the significant problems of stability and catalyst recovery cannot be overlooked. These problems make such systems inapplicable to other areas such as direct coal liquefaction to boiler fuels. The reasons and ramifications for this inapplicability are discussed in detail elsewhere (30).

All of the techniques discussed so far have been directed at preparing highly dispersed supported metal catalysts. The other parameter for consideration is maintenance of metal dispersion. The formation of bimetallic alloys for such a purpose has already been discussed (68) in Section II. The use of metal support interactions (69-70) is also very effective and is detailed in Section III. Two other

procedures which have broad applications should be mentioned.

In one, a trimetallic alloy or cluster is formed to stabilize two normally immiscible metals (71). The primary requirement of the third metal is that it be miscible in both of the other metals. Thus, Ru-Cu "alloys" or clusters can be stabilized by the addition of nickel since the latter metal is miscible in both ruthenium and copper. A stable Ru-Ni-Cu alloy or cluster is formed. Similarly, a stable Ru-Pt-Cu catalyst has been prepared (71).

The second stabilization procedure is one which has recently been developed to prevent macroscopic migration of metal salt solutions during the drying step subsequent to impregnation. For example, such is the problem which accompanies impregnation of monolith substrates with platinum salt solutions. During drying the salt migrates under capillary forces and develops a concentration gradient across the monolith. This leads to uneven catalytic activity (72). This gradient can be eliminated by treating the impregnated monolith with H_2S which converts the impregnating salt to a monodispersed insoluble sulfide (73). The latter cannot migrate during drying. A brief air calcination and subsequent hydrogen reduction gives a highly and uniformly dispersed metal catalyst. The technique has broad applications, and could find use in preparing a wide variety of metallic or multimetallic catalysts.

C. NONMETALLIC CATALYSTS

There are a number of nonmetallic catalysts of interest both for catalysis in general and more specifically for the catalytic conversion of coal. In the latter category, oxides, sulfides, and oxysulfides

find the broadest application (30). Many of the techniques which are used to prepare these materials are similar to those previously described for the preparation of metallic catalysts. In the following discussion, nonmetallic catalysts will be divided into two classes, unsupported and supported.

1. UNSUPPORTED CATALYSTS

High surface area, unsupported catalysts or catalyst supports can be prepared by methods previously discussed such as flame decomposition (12), freeze drying (14-18), sol-gel formation (23-25), gel precipitation (23,26), homogeneous pH control (62, 63), and aerogel formation (27-29). By controlling the various preparative variables for these techniques, surface area, pore-size distribution, and mechanical strength can be varied within broad limits. Most of these procedures lead to oxides or mixed oxides. In some cases, sulfides or oxysulfides can be generated by an appropriate sulfidation treatment. Other chemical treatments can be used to generate alternate materials as well. For example, a combination of freeze-drying and a high temperature treatment of a colloidal graphite-tungstic acid solution has been used to give high surface area tungsten carbide ($d \sim 350 \text{ \AA}$) (14). Similarly, nitrides, borides, and phosphides can be prepared in reasonable surface areas (30, 45-48) using other chemical treatments.

A procedure worth noting is that of impregnation synthesis (74). This technique provides a means for synthesizing novel inorganic compounds which are normally prepared by high temperature solid-state reactions. The later results in low surface area materials which are unacceptable for catalytic testing. In a particular example, it

was desired to synthesize a series of materials with the general formula $M_2Mo_3O_8$ when $M = Mg, Zn, Mn, Cd, Fe, Co, \text{ or } Ni$ (74). A structural feature of these materials is the presence of clusters of three Mo cations bonded together with a Mo-Mo separation of 2.53 Å. This close approach is smaller than the Mo-Mo distance in molybdenum metal, and therefore indicates strong bonding within these clusters. To study the catalytic properties of these materials, it was necessary to prepare them in high surface area. Impregnation synthesis was brought about by impregnating high surface area MgO with $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, followed by calcination in an H_2/H_2O environment at 500-700°C to affect the surface reaction. Excess MgO was removed with dilute HCl. The dried product was pure $Mg_2Mo_3O_8$ with a surface area of 100 m²/g. The general steps for impregnation synthesis involve the use of one reactant as a high surface area template. The subsequent reaction rate to form the surface compound is generally much greater than the corresponding solid state reaction because of the highly dispersed nature of the system, and therefore occurs at significantly lower temperatures. Finally, the excess support or "template" is removed by any number of solubilization techniques. The general procedure of impregnation synthesis should find broad application for preparing new catalytic materials.

2. SUPPORTED SYSTEMS

As with metals, nonmetallic catalytic phases are readily deposited on supports to give high dispersion of the active component and to maintain this dispersion. Oxides of transition metals such as chromium, cobalt, molybdenum, iron, and nickel, among others, are readily supported by all of the procedures previously described for the preparation of supported metal catalysts. The more common techniques

include impregnation procedures (53, 54, 58), adsorption from solution (60, 61), and gel precipitation (23, 26). For example, chromia supported on alumina is readily prepared by incipient wetness impregnation of alumina with an aqueous solution of a chromium salt such as chromium nitrate, ammonium dichromate, or chromic acid (75). The impregnated catalyst is subsequently dried and calcined to give dispersed chromium oxide on alumina. Similar catalysts can be prepared by precipitation procedures by adding a solution of chrome nitrate to a suspension of alumina in ammonium hydroxide (76). Alternatively, chromia-alumina can be prepared by a coprecipitation procedure by the addition of ammonium hydroxide to an aqueous solution of aluminum and chromium nitrates. In general, the impregnation procedure is useful for preparing low weight loadings (1-20 wt.%). For higher loadings (20-60 wt.%) of the catalytic phase, precipitation or gelation procedures are more effective. Similar techniques are used for other transition oxides or mixed oxides.

An example of the preparation of a commercial supported non-metallic catalyst is that of cobalt molybdate on alumina. A recent innovation in this area describes the preparation of a cobalt molybdate catalyst using an alumina support with a controlled pore-size distribution (77). In this case, silica-stabilized alumina with greater than 50 percent of its surface area in 30-80 Å pores, and at least 3 percent of the total pore volume in pores greater than 2000 Å in diameter, was impregnated with an aqueous solution of salts of cobalt and molybdenum. The catalyst was dried, calcined, and presulfided with an H₂S/H₂ mixture to give the final supported oxysulfide catalyst. This catalyst was tested for hydrodesulfurization of petroleum atmospheric residuum at

700°F and 1500 psig for 28 days. It was compared with a conventional cobalt molybdate catalyst having a major portion of the surface area in pores ranging from 30-70 Å diameter. The latter retained 57 percent of its original activity, while the controlled pore catalyst maintained 80 percent activity.

As discussed in Section IV, supported non-metallic catalysts are more difficult to characterize than supported metallic catalysts. This is primarily because there are no broadly applicable selective chemisorption procedures for determining the surface area of the active species. This is in contrast to supported metal catalysts where metal surface area is readily measured by selective adsorption of gases such as O₂, CO, and H₂. While X-ray, magnetic, and various spectroscopic techniques are applicable to non-metallic catalysts, the state of understanding of supported non-metallic systems is behind that for supported metal catalysts.

D. PRACTICAL IMPLICATIONS

It is useful to summarize the key points which have been made in this section, especially as they apply to areas of interest for the catalytic conversion of coal. For convenience, these comments are divided into the same six categories listed in Table V.1.

1. DISPERSED MATERIALS

Numerous new compounds are synthesized by solid-state and inorganic chemists each year. Many of these materials contain elements of catalytic interest, either in preferred oxidation states or in unusual structural forms. A wealth of discovery awaits the catalytic scientist who can prepare certain of these materials in high enough

surface area to be readily amenable to characterization and catalytic testing. Techniques such as impregnation synthesis (74), flame decomposition (12), and freeze drying (14-18) offer a means to fulfill this need for many systems. These and other preparative procedures mentioned in Table V-1 should find broad application for general catalyst preparation. Even if some of these techniques have few commercial implications, they may provide a means for screening new materials in the laboratory in a most expeditious way.

2. SUPPORTED CATALYSTS

While impregnation procedures are fairly well understood, the displacement of immiscible liquid (DOIL) procedure should be further explored. It may provide a means for controlling the extent of deposition of the catalytic phase in a given part of the pore distribution.

An area which will undoubtedly have an impact on the preparation of highly dispersed, supported catalysts is the increased understanding of the nature of the solution chemistry which occurs at the liquid-solid interface during adsorption. This should lead to procedures for preparing metals such as nickel, cobalt, iron, copper, silver, gold, and ruthenium in very high dispersion. Historically, these metals have been difficult to prepare in high surface area. Such an advance would also have a significant impact on the preparation of multimetallic clusters as well (Section II). Applications of this work are expected in the areas of CO/H₂ synthesis and general refining and upgrading of coal liquids.

The anchoring of organometallic complexes may find application in two areas, CO/H₂ synthesis (especially methanation and methanol

synthesis), and more remotely, water-gas shift catalysis. The motivation for this work is based on two assumptions. It assumes that organometallic complexes which catalyze the reduction of CO with H₂ can be synthesized, and that these complexes will be sulfur tolerant. As will be discussed in Part 2, there is some basis for these contentions. Anchored catalysts are usually run in liquid phase. Liquid phase methanation, Fischer-Tropsch, or methanol synthesis has advantages for reasons of heat transfer. This also will be detailed in Part 2.

3. CONTROLLED PHYSICAL PROPERTY SUPPORTS

Advances in this area will be important for preparing support materials with controlled pore-size distributions, optimal surface acidity, and improved mechanical properties. The aerogel technique developed by the French workers (27-29) has significant promise in this respect. Preparative variables are readily controlled, and the method is simple. The synthesis of mixed oxides, sulfides, oxy-sulfides, etc. is also attainable by this procedure. Areas of impact are direct liquefaction, CO/H₂ synthesis, and water-gas shift catalysis. For direct liquefaction, controlled-pore supports have proven to be very useful in extending catalyst life (77). Wide pores are necessary to prevent geometric poisoning by blockage from surface deposited inorganic materials. Small pores give increased surface area for optimum hydrogenation activity. Obviously, a proper balance is required. As discussed in Section III, pore-size distribution can have a marked effect on product distribution for CO/H₂ synthesis reactions. For water-gas shift catalysis, the aerogel technique presents a method of preparing a broad range of novel mixed oxide systems.

4. STABILIZED SUPPORTS

The value of this area for the catalytic conversion of coal cannot be over-emphasized. Many of the pertinent catalytic reactions are very exothermic (e.g. methanation, water-gas shift). In some cases catalysts will have to be oxidatively regenerated. The preparative procedures for thermally stabilizing aluminas and zeolites will have significant value in preparing new catalysts for direct liquefaction and CO/H₂ synthesis reactions. Catalysts for HDS, HDN, and hydrocracking which will tolerate temperatures as high as 1100°C already exist (40-44). The impact in refining and upgrading is therefore apparent.

The technology which has been developed in engineering and materials science, and which has culminated in the development of refractory and monolithic supports may have application for gas-phase reactions in areas where heat and mass transfer are problems (e.g. methanation, Fischer-Tropsch synthesis). These materials open a new dimension for catalysts in terms of heat and mass transfer characteristics, mechanical properties, pressure drops, and other engineering variables. This will be explored in more detail in Part 2.

5. STABILIZED SUPPORTED METALS

As mentioned previously, metals are not likely to be useful as direct liquefaction catalysts. This is because advantage cannot be taken of the metallic properties of these materials since bulk sulfidation is anticipated at the conditions of direct liquefaction. However, as applied to CO/H₂ synthesis reactions, stabilized metals and multimetallic systems are likely to be very important for controlling product distribution and possibly providing added sulfur

tolerance. New stabilization procedures such as the use of bimetallic (55, 56, 68) and trimetallic (71) systems could be very important both in this area and in upgrading and refining of coal liquids. The new metal-support stabilization procedures developed for automotive catalysis (69-70) are also expected to be important for the preparation of thermally stable and sulfur-tolerant catalysts (see Section III).

6. MULTIMETALLIC CATALYSTS

Many of the statements made in the above section apply to this area as well. In addition, it should be noted that much work has been done with Raney metal catalysts, both in packed beds (20, 21) and flame-sprayed (19). The many advances which have been made in multimetallic catalysis over the last several years may well find application in this area as well. Already, multimetallic Raney-type catalysts are being prepared and tested (20).

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VI. POISONING AND REGENERATION

A. INTRODUCTION

The prevention of catalyst poisoning and the necessity for catalyst regeneration present a number of difficult and important constraints for the technical and economic feasibility of most coal conversion processes. These aspects are particularly important for the production of methane or liquids from coal, and may be a determining factor in the type of processes used in the future. The magnitude of the problem parallels the poisoning and regeneration problem encountered in the upgrading of heavy petroleum crudes and vacuum or atmospheric residuum. In the extreme cases of high sulfur, high metal containing oils, for example, the life of a residuum desulfurization catalyst is less than 30 days and no successful regeneration scheme is available to date. The catalyst, however, is relatively expensive (\sim \$1/lb.), and the need to discard it severely affects the economics of the process. Similar poisoning problems may be encountered in certain coal liquefaction processes, and are definitely an important factor in methanation economics.

In spite of the importance of the area of catalyst poisoning and regeneration to coal conversion, only limited progress has been made in the last decade. However, it was felt that poisoning should be part of this study, primarily to highlight the lack of attention it has received in the scientific community and to point to promising directions for research. This section will first briefly mention the primary poisons of concern in coal conversion, and then discuss the nature of poisoning together with regeneration studies in more detail.

B. GENERAL ASPECTS OF POISONING

Two types of effects are considered for catalyst deactivation: fouling and poisoning. Fouling is the result of deactivation due to species that are originally a molecular part of the reactants. These species, therefore, result from transformations of the feed. Carbonaceous residues are a typical example. Poisons, on the other hand, are not originally a chemical part of the reacting material. They are impurities introduced in the feed stream. Examples are H_2S in methanation and Fischer-Tropsch (where the reacting material is CO and H_2), and mineral matter in coal liquefaction. The main reason for distinguishing between these two types of deactivation processes is kinetic, namely the relationship between the rate of the process and the rate of poisoning, as will be shown later in this review.

In the processes of interest in coal conversion, the most severe poisons and fouling agents are sulfur, carbon residues and inorganic materials. In liquefaction, for example, activity decay is caused by the accumulation of carbon on the catalyst as well as the deposition of metal compounds and minerals on the catalyst surface. In the upgrading of coal liquids, carbon again is a primary problem, as is the severe poisoning effects of sulfur. Methanation catalysts are particularly sensitive to H_2S , to the extent that in current processes concentrations of H_2S have to be kept below 1 ppm. The same holds true for Fischer-Tropsch catalysts, where H_2S , carbon residues, and chlorine cause catalyst deactivation.

The main advances in this area over the last decade have been in the modeling of deactivation phenomena as indicated by the many references on this subject (1-11). This work has concentrated on coke

deposition with only limited emphasis on other fouling or poisoning agents. However, as will be seen later, many of the relations that were developed for coke deactivation hold for other deactivation phenomena as well. In the following discussion, studies dealing with sulfur, carbon, and other poisons and metals will be discussed separately.

C. SULFUR

1. GENERAL

The degree of the effect that sulfur compounds have on the catalyst depends on the conditions of the system. Two extreme conditions have to be considered. On one extreme, the bulk composition of the catalytic material is affected. This can occur when large pressures of sulfur-containing molecules are present, and may lead to complete sulfidation. On the other extreme, small amounts of sulfur species compete with the reactants for adsorption sites. In the intermediate case, small amounts of sulfur cause a re-structuring of the catalytic surface, changing the activity to a much larger degree than expected by simple competition for active sites. The extent of any of these processes is a function of the thermodynamics of the catalytic material in the reactive environment. Only few studies of the thermodynamics of materials of catalytic interest in the presence of sulfur have been reported (12, 13). Bulk considerations have been recently included in a review of catalytic materials of interest to coal liquefaction (13). It was found that at the high H_2S levels encountered in liquefaction processes (over 1%), most compounds can sulfide. Exceptions are several oxides (Al_2O_3 , SiO_2 ,

TiO₂) and certain borides, phosphides, and silicides of transition metals. The sulfiding tendency decreases with decreasing severity of the environment. Platinum, for example, is expected to resist bulk sulfidation at temperatures of the order of 400°C in environments of less than 100 ppm H₂S in H₂. Above this pressure, however, strong interaction of H₂S with the metal surface is expected. In the case of Ni at 550°C, for example, a monolayer of sulfur has been observed at concentrations of H₂S in H₂ in the range of 2 to 5 ppm (14). Similarly, for iron catalysts at 400°C, a monolayer has been reported at H₂S concentrations of 1.6 ppm (15). In this latter report, it is noted that only a fraction of the monolayer coverage is required to completely poison the catalyst for ammonia synthesis.

In many other instances it has been observed that sulfur adsorption on a catalyst leads to a change in activity much more pronounced than simple loss of active surface area (16). One of the few papers that have attempted to explain this effect (17) suggests that it is due to a reconstruction of the surface of the catalyst. According to the author, this is a consequence of the difference in surface energy of the various low-index planes of a solid. It is speculated that adsorption of small amounts of H₂S modifies the surface energy balance and leads to a new equilibrium distribution of surface planes with different catalytic activity. Such an explanation has important consequences on the types of reactions that are affected by poisoning by H₂S or other sulfur containing species. Thus, as was discussed in Section III, reactions that are structure sensitive such as hydrogenolysis and isomerization would be affected to a much greater degree by this type of poisoning compared to structure

insensitive reactions such as hydrogenation. This may, in fact, be the explanation for an effect reported recently by Maurel, et al. (18), who report a dramatic difference in the effect of sulfur poisoning on two Pt catalyzed reactions: the hydrogenolysis of cyclopentane and the hydrogenation of benzene. The difference was observed only when both H_2S and SO_2 were introduced in the system. The authors note that the tendency to produce elemental sulfur is highest when the two reactants are introduced together, due to the formation of H_2O . Such effects of poisoning on selectivity will certainly become important aspects of future research in this area.

The complexity of the sulfur poisoning problem becomes clearly apparent when more than one component is present in a catalyst system, since the effect of sulfur will not be uniform. Steam reforming catalysts, for example, usually contain promoters in addition to nickel. Some of the promoters bind sulfur more strongly than others. Thus, Rostrup-Nielsen reports that Na and K will in general form sulfates that cannot be regenerated with steam at $600^{\circ}C$ (14). The unpromoted catalyst, on the other hand, and catalysts promoted with Mg and Ca, regenerate easily at these conditions (14). For shift catalysts such as $CuO - ZnO$, both components have been found to sulfide in H_2S (19). In this case, the shift activity loss was found to correlate with CuO area.

Taking advantage of the reactivity difference of two components of a catalyst system to increase the sulfur resistance of catalysts has been investigated for several applications. The addition of Cr_2O_3 to nickel-zeolite catalysts, for example, has been reported to increase sulfur tolerance for ethane hydrogenolysis (20). This is an effect that should be explored further in the future.

2. KINETICS AND MECHANISM

The studies of the kinetics and mechanism of H₂S poisoning have been limited, for the most part, to the qualitative studies discussed earlier. Several quantitative studies of the kinetics of H₂S adsorption on single crystal surfaces (25, 26), in fact, reveal that for certain metals such as Pt and Cu there are two adsorption regimes. At coverages below 0.5-0.6 of a monolayer, the adsorption is fast with a high sticking coefficient. Above this coverage, the adsorption process slows down considerably, being characterized by a very low sticking coefficient. The nature of this phenomenon is not understood. However, it is clear from these observations that the adsorption of H₂S on a metal surface affects its behavior more severely than expected from mere one-to-one interaction of an H₂S or S molecule with a surface atom. Surface reconstruction, discussed earlier, may be only one possible explanation. An interruption of the continuity of the metal surface may also be an important factor in the behavior of a poisoned catalyst, as well as the possibility that adsorption on one site affects the neighboring sites. Observations that point in this direction and have important practical consequences have been made by Dalla Betta, et al. in their study of methanation (27). As described in more detail in Section III, they find a strong effect of H₂S poisoning on the selectivity of a number of catalysts, including Ni and Rh on various supports. They speculate that the effect is due to the type of site interruption mentioned above. Considerably more work needs to be done in this important area.

Interest in sulfur poisoning models and the mechanism of poisoning by sulfur containing molecules has also been limited. Most

of the fouling or poisoning models in the literature have been applied primarily to carbon deposition. However, as pointed out by Carberry and Gorring (7), they also apply to sulfur poisoning in certain cases. In particular, these authors refer to observations made by Anderson, et al. on iron Fischer-Tropsch catalysts (21). Anderson found that the resistance to sulfur poisoning of the catalyst increases with decreasing pellet size. The sulfur is found in a thin layer near the catalyst surface, which is consistent with the "shell progressive mechanism" that has been applied to carbon deposition on catalyst pellets (7).

3. REGENERATION

The question of regeneration of sulfur poisoned catalysts has been discussed by several investigators (14, 15, 17, 25, 28). As mentioned in Section III, Rostrup-Nielsen (14) finds that regeneration of sulfur-poisoned nickel catalysts varies with the promoters used in the catalyst system. Those promoters that bind sulfur most strongly are the most difficult to regenerate. However, as also discussed in Section III, in certain cases promoters tend to improve the poison resistance of the catalyst. An interesting suggestion concerning this point was made by Somorjai (17). After speculating that small amounts of sulfur result in surface reconstruction of catalysts such as Pt and Ni, he concluded that the addition of compounds that would restore the original surface morphology would enhance sulfur resistance and regeneration. Patents on the subject are not very explicit in procedures or rationale (28).

4. ACTIVITY MAINTENANCE

A final aspect of the interaction of H_2S with a catalyst should

be noted. While the earlier discussion stressed the negative effects of sulfur poisoning, there is one application that makes use of the strong adsorption of H_2S . This is practiced in catalytic reforming, where H_2S is purposely added to a stream to moderate the activity of a Pt or a bimetallic catalyst in order to minimize initial coke deposition (29, 30). The function of H_2S is to minimize hydrogenolysis activity (cracking) which leads to high surface concentrations of unsaturated carbon species. The latter rapidly "polymerize" to coke and give poor activity maintenance.

D. CARBON

1. GENERAL

Catalyst deactivation by carbon deposition is a phenomenon that occurs for most hydrocarbon reactions. In effect, during catalytic reforming, a high H_2 pressure is introduced to minimize coking in spite of its adverse effect on the kinetics of some of the hydrocarbon reactions. In methanation, carbide formation ranks as one of the most severe problems, second only to sulfur poisoning. In hydrodesulfurization, catalyst life is severely limited by heavy carbon deposition, in particular with heavy crudes and residua.

In spite of the universal nature of the problem, only limited attention has been given to the several key questions concerning carbon deposition, in particular the nature of the carbon species. Eberly and co-workers have presented one of the few studies on the subject (1). They investigated the nature of coke on cracking catalysts by infrared spectroscopy, and concluded that the carbon is present as highly condensed, aromatic structures of low hydrogen content.

The situation with coal conversion catalysts is likely to be more complex. In hydrodesulfurization, for example, two distinct deactivation regions are observed (2). It is likely that the nature of the carbon containing residues are different in these two regions. The understanding of this phenomenon would benefit from investigations of the type conducted by Eberly. However, no such investigation has been reported to date. Emphasis in the area of carbon fouling has been primarily on modeling of the catalyst deactivation process and regeneration. These two areas will be discussed separately.

2. MODELING OF DEACTIVATION

Most of the work on coke deposition deals with modeling of the deposition reaction (1-11). Most models use empirical power laws. However, because the coking rate is a function of space velocity (1), simple power laws are applicable only in limited space velocity regions. In expressions of the type

$$C = At^n \quad (1)$$

where C is the weight percent carbon on the catalyst, t is time, and A and n are constants, the value of n can vary anywhere from 0.4 to 1.0 in the 0.2 to 20 V/V/hr space velocity range (1). A diffusion controlled expression, ($n = \frac{1}{2}$), is only expected in a small region of operation. However, in spite of the variation in n , expression 1 has been successful in modeling several systems, in particular zeolite and $\text{SiO}_2/\text{Al}_2\text{O}_3$ deactivation in cracking reactions (2, 4, 31).

Other expressions have been used to describe fouling in cracking reactions. A simple first order decay model,

$$\frac{da}{dt} = Aa \quad (2)$$

where a is the rate of reaction normalized to the initial (unpoisoned) rate, has been as successful in modeling cracking reactions as equation 1 (4, 31). This reflects the inability of these expressions to elucidate the actual fouling mechanism.

Efforts to derive general poisoning equations and to relate parameters to specific deactivation mechanisms have intensified in the last decade (5-7, 9-11). They usually incorporate parallel reactions (fouling due to side reactions of the main reactants), series reactions (fouling due to further reaction of the primary product), and poisoning by species not derived from the reactants.

Equation 2 is, in effect, a limiting case of a general expression, derived by Khang and Livenspiel (5), which incorporates these three types of deactivation mechanisms:

$$\frac{da}{dt} = Aa^d \quad (3)$$

In this expression, the constant d varies from 1 to 3, depending on the controlling mechanism. The value $d = 1$ is obtained for several models, including uniform deactivation (i.e. no diffusion resistance) for both parallel and series reactions (5). The inclusion of diffusion limitations in these models can have a very important effect on the results. In fact, in certain cases discussed by Lee and Butt (11), the presence of some diffusion limitation results in an increase in catalyst life.

One diffusion model of interest, which was mentioned in Section VI-C, is the "shell-progressive" model, where the reactants have to diffuse through a growing non-reactive shell of the catalyst pellet (6, 7). The effect is expected when diffusion resistance is

large compared to the fouling rate, and is found to apply most successfully for parallel fouling reaction (6) as expected from the nature of the deactivation (dependence on reactant concentration). General relationships for this type of mechanism have, in fact, been developed (7). The specific determination of the type of controlling fouling mechanism has been explored experimentally and theoretically by Petersen and co-workers (32-35). By using a single pellet reactor and monitoring the reactant concentration in the exterior and "center plane" of the pellet, the authors were able to determine many of the rate parameters of the reaction. Recently they have extended their computations from first to higher order reaction rates (10). They find that the relative rate is most affected by the order of the reaction in parallel poisoning reactions. It has a minor effect on pore-mouth poisoning models, and also, of course, on poisoning by impurities.

This type of elucidation of poisoning and fouling phenomena is an important aspect of the area discussed in this section, especially because it relates to both the modification of catalysts for increased resistance to deactivation and to the design of new regeneration schemes.

3. REGENERATION

In spite of the importance of regeneration of coked catalyst to the coal conversion industry, it has received only minor attention in the R & D community. This may be indicative of the complexity of the problem. In the petroleum industry, the regeneration of coked catalysts is commonly achieved by controlled slow oxidation of the carbon. In the absence of diffusion effects, this regeneration has been found to be first order in O_2 and C (36). The kinetics of carbon combustion under completely diffusion controlled conditions is more

complex (37). For coal conversion, where the problem is particularly severe, other poisons such as coal ash, mineral matter, and metals are also present (38). These additional poisons cause irreversible complications during oxidative regeneration, which have not been fully explored to date. It is an area that requires an increasing research effort, in particular with coal conversion processes where the ash problem and the presence of metals such as Ti are likely to be important (39). Efforts to identify the effect and importance of these poisons will be discussed in the next section.

E. OTHER POISONS

In addition to carbon and sulfur, the poisons of most concern in petroleum and coal processing are mineral matter (salts such as NaCl) and metals such as V, Ni, and Ti (39). In certain reactions that are catalyzed by acid sites (zeolites or $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts), nitrogen compounds also present a serious problem (40, 41).

The literature on metal poisons is limited to confirmation of the effect. Little is known concerning the specific poisoning mechanism or the nature of the poisons on the catalyst surface. In particular, for coal processing, the poisoning effects of alkali containing salts and Ti have only recently been confirmed (39). The effect of similar species for petroleum processing (in particular V) have also now been established (38). The effect of these poisons is felt primarily in regeneration. Catalysts used in low metal, low mineral containing feeds can be regenerated by the oxidative procedure mentioned earlier (38, 39). However, when the metal poisons are present, the only regeneration procedures that have been suggested involve complete extraction of the metal catalysts from the support (42).

F. CONCLUDING REMARKS

The development of effective catalyst regeneration schemes are expected to become more critical as the importance of coal conversion and upgrading increases. It will become an important economic consideration in the choice of conversion system. The current understanding of the effect of most fouling agents and poisons is limited, and alternative regeneration strategies are practically non-existent. An increased effort is needed for the development of regeneration procedures for HDS catalysts poisoned by the alkali metals, vanadium and titanium contaminants. The nature of these poisons has to be established, and the real extent of their interference with traditional regeneration procedures clarified. A similar effort is required to develop sulfur tolerant methanation catalysts if this route of coal conversion is to be economically viable. The impact of some of the key advances in catalysis on this problem has been explored in many of the preceding sections of this study.

In particular, there is a need for a better understanding of the interaction of poisons and fouling agents with the catalyst and the support. The reasons for the large changes in surface area upon oxidative regeneration of Na and V containing HDS catalysts, for example, may be linked with solid-state reactions which could be inhibited or avoided. However, this cannot be achieved until the nature of the interaction is clarified. In the case of sulfur, the efforts to develop tolerant catalysts would benefit considerably from an understanding of the solid-state and surface chemistry of the S-catalyst systems. Similarly, effects such as S-induced surface reconstruction and selectivity changes should be explored further since they may have important implications on processes such as methanation and Fischer-Tropsch synthesis.

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