III. EFFECTS OF CATALYST-SUPPORT INTERACTION, PARTICLE SIZE, AND SURFACE MORPHOLOGY

A. INTRODUCTION

Two areas which affect catalyst behavior have attracted increasing attention over the last decade: catalyst-support interactions and the role of catalyst morphology and structure on activity. Attention has focused on both the fundamental and the practical aspects of these areas, resulting in a better understanding of many catalytic reactions and the development of new and improved catalysts. They are therefore areas of considerable interest for this study. Progress in these areas have benefited considerably from the ability to characterize catalysts, in particular in terms of the surface area of the active species. Characterization will be discussed in Section IV. In this section the most recent developments in structure sensitivity and catalyst-support interactions will be highlighted, and general implications of these developments discussed.

B. GENERAL COMMENTS

The surface area of a catalyst is increased by decreasing particle size. The surface area of the small particles is maintained by supporting them on high surface area substrates. Both the small particle size and the support can induce physical and chemical changes in the catalyst. These changes are closely related to the catalytic behavior of the catalyst particles. Changes in the particle size of a metal, for example, lead to changes in the distribution of exposed faces, surface irregularities, steps and edges which play an important role in certain reactions. Furthermore, the change in particle size may lead to changes in the phase properties of catalysts, in particular in multiphase systems such as the multimetallic systems discussed in Section II. These chemical changes become more significant as the particle size decreases. They are paralleled by increasing interaction of the catalyst with the support, and more prominent roles of additives in modifying the properties of the catalyst. The same holds true for the support, which by virtue of its high surface area is composed of very small particles (100-200 Å). These two factors, namely catalyst-support interactions and the effect of particle size, will be discussed separately. However, it should be noted that they are closely related, as will become clear in many of the examples that will be reviewed.

C. CATALYST-SUPPORT INTERACTION AND STABILIZATION

One of the most important concerns for catalytic reactions is the loss of activity due to a decrease in active surface area by agglomeration or catalyst loss. It is particularly severe in exothermic reactions such as methanation and methanol and Fischer-Tropsch synthesis. In these reactions, loss of surface area of the catalytic material not only leads to a decrease in performance, but also often results in a change in product distribution. The problem is not limited to the active catalyst. It extends to catalyst support, which can sinter under severe reaction or regeneration conditions.

In the last decade there has been an increasing attempt to prevent surface area loss by the addition of stabilizing components to a catalyst system or by proper choice of catalyst-support interactions. These two approaches will be discussed separately.

1. ADDITION OF STABILIZING COMPOUNDS TO CATALYST SYSTEMS

The use of compounds to improve the thermal stability of a catalyst is not new. In ammonia synthesis, for example, Al_2O_3 has been used as a "structural promoter" of the Fe catalyst for many years. It is believed to form small domains within the Fe particles, thus preventing agglomeration (1). Examples of such structural promotion has been encountered in other systems (for example CrO_3 in the Ni catalyzed dehydrogenation of isopropanol (2)). It is probably more prevalent in multiple-compound catalysts than is currently recognized.

The emphasis in this area of structural stabilization has been concentrated in the last few years on the addition of small amounts of certain oxides to supports. Oxides tested include CuO, MoO_3, V_2O_5, Cr_2O_3, TiO_2, SiO_2, CdO, ZnO, CaO_2, and MgO (3). While the addition of CuO, MoO_3 and V_2O_5 leads to a dramatic loss in surface area after heating to 1000^oC for 24 hours, MgO, SiO_2 and CeO stabilized the area of the support. Surface areas as high as 30 m^2/g^{-1} at 1200^oC have been reported. Some of these additives also increased the crush strength of the pellets, an important parameter for many catalytic applications. As will be discussed later, it is believed that delay in the transformation to α-Al_2O_3 is often responsible for the stabilization. In the case of surface area loss in the presence of MoO_3, the formation of aluminum molybdate at 600^oC and decomposition to α-Al_2O_3 and MoO_3 at 800^oC are believed to be responsible for the severe surface area loss indicated earlier (3).

Stabilization of alumina by spinel forming elements has been observed in other cases as well. A study of the effect of Mo and Co impregnated on alumina, for example, showed that the presence of Co inhibits sintering (4). In contrast, Mo enhances sintering, and the presence of both metals results in an intermediate effect. The tests were performed in a temperature range of 700-900°C. It is interesting to note that of the two transition metals, only Co forms a compound (spinel) with Al_2O_3. However, in general it is difficult to predict the direction of the stability change of a material in the presence of other ions. Often the presence of impurities enhances phase transformations with concomitant surface area loss. In the TiO_2 system, for example, the anatase-rutile transformation is accelerated considerably by the presence of elements such as Cu, Mn, and Fe (5). Conversely, the presence of B_2O_3 in Al_2O_3 has been claimed to inhibit the formation of α-Al_2O_3 (6). In zeolite catalysts the question of stability has been of particular concern, since many zeolite forms are temperature sensitive, especially in the presence of water. Recently, patents have appeared claiming ultra-stability, in some cases under hydrothermal conditions. The addition of rare earth cations, fluorine ions, Mg, and exchange of Na^+ for NH_4^+ in NaY and NaX zeolites are claimed to result in zeolites stable to temperatures greater than 800°C (7, 8). This is a considerable improvement over the untreated zeolites, whose surface area and structural integrity decreased rapidly at temperatures in excess of 500°C, in particular in the presence of steam. The new zeolites should have wider applicability, particularly in processes in which the reaction or regeneration occurs at high temperatures in the presence of steam. High stability can also be achieved by careful removal of Al, in effect leading to a structural change. For example, Kerr (9) found that a hydrogen zeolite, Type Y, heated 2-4 hours at 700-800°C in an inert atmosphere where the chemical water remains in the environment of the hydrogen zeolite, yields a new zeolite with remarkable thermal stability, even capable of enduring temperatures as high as 1000°C. He showed that in the new structure approximately 25% of the aluminum was present in the cationic form (10). He also found that the removal of aluminum from sodium Y zeolite through the use of dilute solutions of ethylenediaminetetraacetic acid produced a zeolite with improved thermal stability and increased sorptive capacity (9). Furthermore, bed geometries which impede the removal of ammonia from ammonium Y zeolite during heating give an ultrastable zeolite. The mechanism of stabilization is not completely understood, but is attributed to the removal of tetrahedrally coordinated aluminum. This causes a contraction of the unit cell and an increased structure stability.

2. CATALYST-SUPPORT INTERACTIONS

The above discussion deals primarily with the thermal stability of the support. As mentioned in the introduction, another important factor in the stabilization of catalysts is the effect of the support on the active catalyst phase. Two areas have been explored in this regard: the choice of supports or support components to minimize aggregation of the catalytic material, and the addition of a solid to the support to eliminate or minimize loss of the catalytic phase during use or regeneration. Both are related, and rely on a chemical interaction of the components. This interaction results in a thermal stabilization of the catalyst and a change in its catalytic properties. These two effects will be discussed separately.

a. Thermal Stability

The stability of a catalyst depends critically on the environment in which it is used. Thus, in an oxidizing environment, the stability of a metal such as Ni or Ag on an oxide support is greater than in a reducing environment (11). This is due to the enhanced interaction of the oxidized surface of the metal with the support. Such a stabilization in an oxidizing environment, however, may be overshadowed by a tendency of the metal oxide to volatilize. Ruthenium catalysts are a particularly dramatic example of this effect, while it is also seen to a lesser extent with the noble metals. Among the latter, it is observed that Pt will agglomerate much more severely in an oxidizing vs. reducing environment (12, 13). This is primarily due to the formation of volatile PtO_2. However, it is also argued that in a reducing environment some reduction of the Al_2O_3 surface leads to stronger $Pt\text{-}Al_2O_3$ interaction (11). The degree of this interaction varies with the support. For Ni, for example, Geus shows in his recent review that the energy of interaction varies from 1.5 kcal g-atom^{-1} for Ni/BeO to 7.3 kcal g-atom^{-1} for Ni/ThO_2. It also varies with the metal: 3.5 kcal g-atom^{-1} for Ag/Al_2O_3, 5.2 kcal g-atom^{-1} for Ni/Al_2O_3, and 6.5 kcal g-atom^{-1} for Fe/Al_2O_3. It should be noted that the observed energies are of the order of typical physisorption energies, thus pointing to rather weak interactions in these cases.

The studies that give data of the energetics of solid-state interactions are very few, and it is therefore difficult to compare the above quoted energies with those of other systems. Most reports are qualitative. Several Russian authors have reported stabilization of supported Pt catalysts by the addition of rare earth elements (14) or even by the addition of Re (15). In the latter case, which involved both Pt and Pd on SiO_2, the degree of reduction of the Re was not established. When comparing Al_2O_3 vs. SiO_2, it should be noted that there is a distinct effect of the support on the dispersion. This has been observed for several metals, including Pt (16) and Ru (17).

It was mentioned earlier that loss of catalyst due to volatilization of the oxide can be a severe problem for some systems. As will be seen in Part 2 of this study, this is also one of the mechanisms that operates in the sintering of metals. In the case of Ru, however, loss of catalyst in an oxidizing environment, and not sintering, is of primary concern, in particular for the use of this metal for NOx reduction in automotive exhaust. While the main reaction occurs in a reducing environment, oxidizing transients cannot be avoided. The solution of this problem provides a good example of the application of the solid state chemistry of the components of a catalyst system, and the use of catalyst support interactions. Two supports have been used: BaO and MgO. They highlight two different but related effects. In the case of BaO, pioneered by the Ford workers (18), Ru and BaO interact under oxidizing conditions to form a ruthenate, $BaRuO_3$. Under reducing conditions, Ru returns to the metallic state and is available for the catalytic reaction. Other ruthenate forming compounds have been used, including the rare earth oxides. The problem one encounters in these materials is durability, partly related to cycling between ruthenate and ruthenium metal. The use of MgO overcomes this problem. Mg does not form a bulk ruthenate. However, a surface interaction appears to occur between the finely dispersed Ru and the MgO which inhibits sintering and minimizes RuO_4 volatilization (19, 20). The presence of a surface rather than bulk effect insures ready availability of the Ru and appears to avoid structural degradation.

b. Surface Chemistry

In addition to changing thermal stability, additives and supports can alter the chemistry of catalytic materials. This can manifest itself in a change in reduction characteristics of the catalyst and in catalytic activity as well. The former is particularly dramatic for non-noble metals. For Ni steam reforming catalyst, for example, it is found that reducibility becomes easier as the concentration of Ni on the support increases (21, 22). The limit, of course, is unsupported Ni. To achieve reduction, lower H_2/H_2O ratios are required for the unsupported material. A similar effect is observed in the thermal decomposition of chloroplatinic acid. Unsupported chloroplatinic acid starts decomposing at 100°C, and is completely decomposed at 550°C (23). On the other hand, temperatures as high as 760°C are required for catalyst supported on alumina (13). The effect differs on different supports, as seen in the study of the reducibility of chloroiridic acid on various oxides (24). By following the photoelectron spectra of the iridium chlorine complex, the reducibility sequence $ZnO < SiO_2 < TiO_2 < Al_2O_3$ was observed. It is interesting that this is the same sequence as expected from the acidity of the supports (25).

A change in the catalytic properties of a metallic catalyst as a function of the support has been discussed in the literature for many years, in particular through the work of Schwab and co-workers (26, 27, 28). The effect that was anticipated by these authors was the influence of the electronic population of the oxide support on the metallic catalyst. By varying the electron population of the support through doping, a variation in the catalytic properties was expected. The results of this work, however, showed that the effect of these variations was too small to significantly alter the catalytic behavior of the system. Nevertheless, an effect of dopant was seen on the activation energy for the dehydrogenation of formic acid over nickel, copper, and silver (27). The effect is especially detectable for thin metal layers. A similar observation was made earlier by Selwood and co-workers (29, 30). They found that compounds deposited on substrates in thin layers are influenced in their properties by the substrate. In the work by Selwood, the influence of the substrate on the structure of a thin oxide film was examined. It was found that in several cases the overlayer assumed the substrate structure, and exhibited a valence state that was not the expected stable state of the particular oxide. However, more than just the need for small dimensions is required, and the chemical properties of the overlayer also influence this behavior.

From the information summarized by Geus (11), and discussed earlier, it can be concluded that the effect of an oxide substrate is most significant on an oxide catalyst. This agrees with Selwood's observations. Other cases of this strong oxide-oxide interaction have been reported recently. Ross and Delgass, for example, examined the change in properties of europium oxide supported on Al_2O_3 or SiO_2, compared to the unsupported material (31). The test reaction was the reverse of the water-gas shift reaction, and the chemical state of europium was monitored by Mössbauer spectroscopy. The behavior of the catalyst was dramatically different for the supported and unsupported cases in one aspect: the effect of CO_2 pressure on the kinetics. The rest of the kinetics, including a proposed surface oxidation-reduction mechanism, was the same. Preliminary Mössbauer information suggested the presence of strong support interaction. Similar strong interactions have been reported by Cimino and co-workers (32) in an investigation of N_2O decomposition on a number of solid solutions of the oxides of Co, Cu, and Ni supported on MgO and ZnO. However, while a strong support effect is encountered in this investigation, the interpretation is complicated by the participation of the so-called support in the reaction.

A final example of a support effect on catalytic activity that is relevant to the present discussion is a recently completed methanation study of Dalla Betta and co-workers (33). Catalysts studied were Raney nickel and Ni supported on ZrO_2 and Al_2O_3. Steady state data were obtained for these catalysts. It was found that the activity per unit surface area of Ni followed the order Ni > Ni/Al_2O_3 > Ni/ZrO_2. However, the reverse order was found for the sulfur tolerance of these catalysts. The significant aspect of this study is that the catalysts were compared on a specific activity basis, i.e. activity per unit area of nickel. In the absence of such a comparison, the results would have been meaningless, in particular since the dispersion of the various catalysts tested varied significantly. This poses a question with respect to the effect of particle size on the reaction, which is the topic of the general area that will be discussed next.

D. EFFECTS OF SURFACE STRUCTURE AND PARTICLE SIZE

1. GENERAL CONCEPT

As mentioned in Section III-B, the support can influence the behavior of a catalyst, in particular when the latter is present as small particles. There is, however, an additional factor that has to be considered in the examination of the catalytic behavior of small particles. It relates to the change in structure with particle size, an effect that has been recognized by the catalytic chemist only within the last ten years (34, 35). An extensive study of the structure of small particles published by Van Hardeveld and co-workers (36, 37), showed that the surface of a particle departs from its characteristic large-particle morphology when it reaches 100 Å, and that the most marked changes occur in the 40-15 Å range. The effect of particle size in this range is a change in the coordination of a surface atom. The equilibrium surface of a large crystallite of an fcc metal, for example, has predominantly 9-coordinated surface sites. An atom adsorbed on such a site has at most 3 nearest neighbors. As the particle size decreases, the number of these sites decreases. A 14 Å crystal, in fact, will have only 33 percent of such sites (38). As the number of high coordination sites decreases, the number of sites which provide 5 nearest neighbors to an adsorbed atom increases to reach a maximum around 20-25 Å (37). This has a strong effect on the surface properties of the crystallite. It should be noted, however, that catalyst particles are not necessarily at equilibrium under reaction conditions. Thus, the existence of metastable surface arrangements or surface reconstruction due to impurities or reactants may also lead to modifications in catalytic behavior. One example of the latter effect will be discussed more extensively in Section VI, namely the effect of small amounts of S impurities on the change in surface energy of a catalyst, and therefore possible surface reconstruction (39).

When one studies the effect of surface changes in catalysis, reactions fall into two categories, as originally classified by Boudart (38); facile and demanding. Facile reactions are those that are not affected by structural changes of the catalyst in the critical region of 20-100 Å. Demanding reactions, on the other hand, require special coordinations or arrangements on the catalytic surface, and therefore depend on the morphology and structure of the catalyst. Examples of these two types of reactions will be discussed next.

2. SPECIFIC EXAMPLES OF PARTICLE SIZE EFFECTS

The last decade, and in particular the last five years, have seen considerable activity in the area of the structure sensitivity of reactions. The interest has centered primarily on the effect of particle size (34, 36, 38, 40, 41, 42-58). Only some studies were directed at the problem more specifically in terms of surface structure (59-62) and the possibility of structural rearrangements with changes in the conditions of the environment or pretreatment (63).

Many reactions do not depend on particle size. Among them one finds hydrogen-deuterium exchange and the hydrogenation and dehydrogenation of hydrocarbons (38). The hydrogenolysis of cyclopentane has also been reported to be a facile reaction (38), however most hydrogenolysis are structure sensitive (64,65). The reactions of neo-pentane offer an example that illustrates the concept of structure sensitivity (65). In the presence of hydrogen, two parallel reactions are expected: isomerization and hydrogenolysis to smaller hydrocarbon fractions. Several arguments indicate that the isomerization to isopentane requires special sites available only on (111) planes or arrangement of sites leading to such planes (66, 34). When isomerization occurs on such sites, cracking is minimized. Therefore, changes in particle size that lead to (III) planes are expected to increase the selectivity to isomerization. This is indeed observed on supported Pt catalysts (34), and is particularly dramatic after a heat treatment that leads to a higher density of (111) surfaces. Such an effect of surface reconstruction has been observed in other systems as well. In the synthesis of ammonia, for example, the activity of a Fe/MgO catalyst increases after treatment in nitrogen (63). The effect is observed only for large particles (300 Å) suggesting reconstruction of surface sites that are not present in smaller Fe crystallites.

A variation in the catalytic activity of demanding reactions has been demonstrated quite clearly in several other examples. In the elegant experiments of Somorjai, et al. (61), for example, the demanding nature of the dehydrocyclization of n-heptane was studied. By using single crystals cleaved systematically to show various well characterized surfaces and steps, these workers found that, in the presence of hydrogen, the rate of this reaction is higher on stepped surfaces of (111) orientation than on corresponding surfaces with (100) orientation. The hydrogenolysis of ethane is also a demanding reaction, as shown by Sinfelt and co-workers for Ni and Rh (67, 68). For Ni, the specific rate was measured over a number of supported samples with particle sizes increasing from 29 to 88 Å (67). A decrease in specific activity by a factor of 20 was observed in this range, with the most pronounced decrease occurring between 29 and 57 Å. This is in line with the discussions of Hartog (37) presented earlier. A similar effect of particle size was observed for Rh (68).

As seen from the discussion so far, the effect of particle size on activity is observed in a number of different reactions, including hydrogenolysis, isomerization, and ammonia synthesis. There is preliminary evidence that methanation, in fact, is also a structure sensitive reaction (33). Dalla Betta, et al. found that the specific methanation activity for Ru increases with increasing particle size at steady state. It is not clear how the variation in catalyst poisoning due to carbon formation as a function of particle size affects this conclusion. Studies of the poisoning effect of H_2S on these catalysts, however, tend to support the particle size effect: the introduction of H_2S alters the product distribution by increasing the content of heavier hydrocarbons in the feed. The authors suggest that this is an indication of increased carbon-carbon bond forming activity with the interruption of the continuous metallic surface, an effect that would be paralleled by smaller particles. This phenomenon may have important implications in coal conversion reactions. These implications, as well as those of the other areas discussed above, are presented in the next section.

E. PRACTICAL IMPLICATIONS

1. CATALYST SUPPORT INTERACTION AND STABILIZATION

The importance of this area cannot be overemphasized. The improvement in the thermal stability of supports and the sintering resistance of highly dispersed catalysts has broad implications for most coal conversion related technology, from methanation and Fischer-Tropsch to HDS and HDN. In fact, catalyst sintering during reaction is one of the most severe methanation problems. At the other side of the spectrum, support sintering during regeneration, in particular in the presence of steam, is a potential problem of desulfurization catalysts and many catalysts used in upgrading hydrocarbon liquids.

The effect of a support on activity and selectivity may, on the other hand, be only of secondary importance. The variation of the activity of different metals is often so large that it masks any improvements achieved by variation in the support formulation unless the support itself is an active participant in the catalytic process. However, there are some reactions where the change may be significant. In methanation, for example, it was mentioned earlier that the support has an effect on the sulfur tolerance of Ni-catalysts without large effects on the specific activity. Such a selective weakening of the interaction of the catalyst with a poison is a very desirable effect, and offers one method for improvement of poison sensitive catalysts.

2. EFFECT OF STRUCTURE AND PARTICLE SIZE

The effects of particle size are closely related to those discussed above. In effect, as the particle size decreases, it is likely that support interactions become more important. However, again the magnitude of the particle size effect on certain reactions has to be kept in perspective. As pointed out by Sinfelt, for example, for the hydrogenolysis of ethane this is a minor contribution compared to the dramatic activity change encountered among different metals (64). Therefore, the importance of the particle size effect is limited to increasing the understanding of the role of the catalyst in the reaction, and has only indirect practical significance.

The difference between demanding and facile reactions, on the other hand, is of great significance. This is particularly true in reactions such as hydrogenation, where the undesirable hydrogenolysis reactions are much more structure sensitive. Small variations in the arrangement of sites may, therefore, affect hydrogenolysis considerably without much effect on hydrogenation activity. This effect is, in fact, observed as was described in detail in Section II, and has wide ranging applications to petroleum processing.

The effect of particle size on selectivity is also likely to be important in methanation and Fischer-Tropsch. The work of Dalla Betta, et al. (33) suggests a change in higher molecular weight hydrocarbons with decreasing particle size for Ru. A maximum is observed at 24 Å, similar to the effect observed by Yates and Sinfelt for ethylene hydrogenolysis on rhodium (68). A picture emerges where particle size has an effect on selectivity and sulfur tolerance of the methanation catalyst. This is clearly an interesting area for further research. Whether these concepts apply to high pressure operation remains to be determined, in particular in light of the recent work of Kreindel, et al. (69). The latter work suggests that the effects of support interactions and particle size effects on methanation activity are insignificant at high pressures. Therefore, these Russian workers claim, only catalyst maintenance is important.

Sulfur impurities can affect not only the continuity of available sites on a surface, but also surface structure. Thus, the possibility of surface reconstruction, as suggested by Somorjai (39) may be an important factor in the poisoning sensitivity of demanding reactions. This is then another area concerned with structure and particle size that should be considered.

F. REFERENCES

1. Boudart, M., Topsøe, H., and Dumesic, J. A., J. Catal. 28, 477 (1973).
2. Mears, D. E., and Boudart, M., AIChE J. 12, 313 (1966).
3. Gaugin, R., Graulier, M., and Papee, D., in Catalysts for the Control of Automotive Pollutants (J. McEnvoy, Ed.). Advances in Chemistry Series 143, p. 147. Amer. Chem. Soc., Washington, 1975.
4. Ratnasamy, P., Mehrotra, R. P., and Ramaswamy, A. V., J. Catal. 32, 63 (1974).
5. MacKenzie, K. J. D., Trans. J. Br. Ceramic Soc. 74, 77 (1975).
6. McArthur, D. P., U. S. Patent No. 3,883,442 (1975).
7. Elliott, C. H., Jr., German Offen. 2,227,334, June 7, 1971; U. S. Appl. 150,780, June 7, 1971.
8. Kerr, G. T., Advan. Chem. Ser. 121, 219 (1973).
9. Kerr, G. T., J. Phys. Chem. 73, 2780 (1969).
10. Kerr, G. T., J. Phys. Chem. 71, 4155 (1967).
11. Geus, J. W., International Symposium on a Scientific Basis for Catalyst Preparation, Brussels, October 14-17, 1975.
12. Baker, R. T. K., Thomas, C., and Thomas, R. B., J. Catal. 38, 510 (1975).
13. Mills, G. A., Weller, B., and Cornelius, E. B., Proc. 2nd. Int. Congr. on Catalysis, 1960, Technip, Paris, p. 2221, 1961.
14. Kozlov, N. S., Sen'kov, G. M., Zaretskii, M. V., Davidovskaya, A. M., and Palei, S. V., Dokl. Akad. Nauk B. SSSR 18, 621 (1974).
15. Bursian, N. R., Kogan, S. B., Semenov, G. I., and Levitskii, E. A., Kinet. Katal. 15, 1608 (1974).
16. Cusumano, J. A., Dembinski, G. W., and Sinfelt, J. H., J. Catal. 5, 471 (1966).
17. Vedenyapin, A. A., Klabunovskii, E. I., Talanov, Yu. A., and Sokolova, N. P., Kinet. Katal. 16, 436 (1975).
18. Shelef, M., and Gandhi, H. S., Platinum Metals Rev. 18, 2 (1974).

19. Deluca, J. P., Murell, L. L., Rhodes, R. P., and Tauster, S. J., presented at Amer. Chem. Soc. Annual Meeting, Chicago, 1975.

20. Bernstein, L. S., Japan-U.S.A. Seminar on Catalytic NOx Reactions, Susono, Japan, Nov. 2-4, 1975.

21. Rostrup-Nielsen, J. R., <u>Steam Reforming Catalysts</u>, p. 42. Danish Technical Press, Inc., Copenhagen, 1975.

22. Ross, J. R. H., and Steel, M. C. F., Trans. Faraday Soc. <u>69</u>, 10 (1973).

23. Shubochkin, L. K., Gushchin, V. I., Larin. G. M., and Kolosov, V. A, Zh. Neorg. Khim. <u>19</u>, 460 (1974).

24. Escard, J., Pontvianne, B., and Contour, J. P., J. Electron Spectrosc. Relat. Phenom. <u>6</u>, 17 (1975).

25. Tanabe, K., <u>Solid Acids and Bases</u>. Academic Press, New York, 1970.

26. Schwab, G. M., Angew. Chem. <u>73</u>, 399 (1961).

27. Schwab, G. M., Block, J., and Schultze, G., Naturwiss. <u>44</u>, 482 (1957; Angew. Chem. <u>71</u>, 101 (1959).

28. Schwab, G. M., Mutzbauer, G., Z. Phys. Chem. <u>32</u>, 367 (1962).

29. Hill, H. F., and Selwood, P. W., J. Amer. Chem. Soc. <u>71</u>, 2522, (1949).

30. Selwood, P. W., Bull. Soc. Chim. Fr. No. 3-4, 167 (1949).

31. Ross, P. N., Jr., and Delgass, W. N., <u>J. Catal</u>. 33, 219 (1974).

32. Cimino, A., Pepe, F., and Schiavello, M., in <u>Catalysis</u> (J. W. Hightower, Ed.), p. 125. North-Holland, Amsterdam/London, 1973.

33. Dalla Betta, R. A., Piken, A. G., and Shelef, M., J. Catal. <u>40</u>, 173 (1975).

34. Boudart, M., Aldag, A., Ptak, L. D., and Benson, J. E., J. Catal. <u>11</u>, 35 (1968).

35. Poltorak, O. M., and Boronin, V. S., Zh. Fis. Khim. <u>40</u>, 2671 (1966).

36. Van Hardeveld, R., and Hartog, F., in <u>Advances in Catalysis</u> (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 22, p. 75. Academic Press, New York, 1972.

37. Van Hardeveld, R., and Hartog, F., Surface Sci. 15, 189 (1969).

38. Boudart, M., in <u>Advances in Catalysis</u> (D. D. Eley, Herman Pines, Paul B. Weisz, Eds.), Vol. 20, p. 453. Academic Press, New York, 1969.

39. Somorjai, G. A., J. Catal. 27, 453 (1972).

40. Cece, J. M, and Gonzalez, R. D., J. Catal. 28, 260 (1973).

41. Primet, M., Basset, J. M., Garbowski, E., and Mathieu, M. V., J. Amer. Chem. Soc. 97, 3655 (1975).

42. Pusateri, R. J., Katzer, J. R., and Manogue, W. H., AIChE J. 20, 219 (1974).

43. Ostermaier, J. J., Katzer, J. H., and Manogue, W. H., J. Catal. 33, 457 (1974).

44. Corolleur, C., Gault, F. G., Juttard, D., Maire, G., and Muller, J. M., J. Catal. 27, 466 (1972).

45. Dautzenberg, F. M, and Plateeuw, J. C., J. Catal. 24, 364 (1972).

46. Dumesic, J. A., Topsøe Khammouma, S., and Boudart, M., J. Catal. 37, 503 (1975).

47. Luss, D., J. Catal. 23, 119 (1971).

48. Cha, D. Y., and Parravano, G., J. Catal. 18, 200 (1970).

49. Carrà, S., and Ragaini, V., "Structure and Catalytic Behavior of Supported Metals", presented at the 20th International Congress "Chemistry Days" on Industrial Catalysis, Milan, May 19-21, 1969.

50. Bond, G. C., Proc. Int. Congr. Catal., 4th, Moscow, 1968, (Paper 67), 266 (1971).

51. Anderson, J. R., and Shinioyama, Y., in Catalysis (J. W. Hightower, Ed.), Vol. 1, p. 695. North Holland/American Elsevier, Amsterdam/New York, 1973.

52. Coenen, J. W. E., Van Meerten, R. Z. C., and Rijnten, H. th., in Catalysis (J. W. Hightower, Ed.), Vol. 1, p. 671. North Holland/American Elsevier, Amsterdam/New York, 1973.

53. Oliver, R. G., and Wells, P. B., in Catalysis (J. W. Hightower, Ed.), Vol. 1, p. 659. North Holland/American Elsevier, Amsterdam/New York, 1973.

54. Maire, G, Corolleur, O., Juttard, D., and Gault, F. G., J. Catal. 21, 250 (1971).

55. Gustafson, W. R., and Kapner, R. S., presented at the Symposium on Recent Advances in Kinetics and Catalysis, Part II, AIChE Sixtieth Annual Meeting, New York, 1967.

56. Boudart, M., and Peak, L. D., J. Catal. 16, 90 (1970).

57. Presland, A. E. B., Price, G. L., and Trimm, D. L., J. Catal. 26, 313 (1972).

58. Clarke, J. K. A., McMahon, E., and O Cinneide, A. D., in Catalysis (J. W. Hightower, Ed.), Vol. 1, p. 685. North Holland/American Elsevier, Amsterdam/New York, 1973.

59. Kahn, D. R., Peterson, E. E., and Somorjai, G. A., J. Catal. 34, 294 (1974).

60. Boudart, M., Delbouille, Derouane, V., and Walters, A. B., J. Amer. Chem. Soc. 94, 6622 (1972).

61. Somorjai, G. A., Joyner, R. W., and Lang, B., Proc. Roy. Soc. 331, 335 (1972).

62. Derouane, E. G., Indovina, V., Walters, A. B., and Boudart, M., in Reactivity of Solids, p. 703. Chapman and Hall, Ltd., 1972.

63. Dumesic, J. A., Topsøe, H., and Boudart, M., J. Catal. 37, 313 (1975).

64. Sinfelt, J. H., Catal. Rev. 3, 175 (1969).

65. Boudart, M., and Peak, L. D., J. Catal. 16, 90 (1970).

66. Anderson, J. R. and Avery, N. R., J. Catal. 5, 449 (1966).

67. Carter, J. L., Cusumano, J. A., and Sinfelt, J. H., J. Phys. Chem. 70, 2257 (1966).

68. Yates, D. J. C., and Sinflet, J. H., J. Catal. 8, 348 (1967).

69. Kreindel, A. I., Sobolevskii, V. S., Golosman, E. Z., and Yakerson, V. I., Kinet. Katal. 15, 408 (1974).

IV. CHARACTERIZATION

A. INTRODUCTION

The preceding two sections pointed out that the increased understanding of catalytic phenomena and the development of new concepts in catalysis in the last decade have depended on the ability to characterize catalytic materials. In addition to being important in these areas, characterization is a key part of catalyst quality control, activity maintenance, and regeneration. The problem of characterization, however, is a complex one. Most catalysts are composed of a number of materials that have individual functions, and therefore require individual identification. Catalysts are usually present as small particles that are beyond the reach of standard materials-analysis equipment. Furthermore, heterogeneous catalysts involve surface phenomena, and therefore bulk parameters have only limited utility in characterizing these systems.

In spite of the complexity, it is now possible to measure a large number of physical and chemical properties for catalysts. Among these are total surface area, pore volume, pore size distribution, the surface area of individual components of a catalyst (specific surface area), surface composition, and, in certain cases, microscopic surface morphology. The determination of total surface area, pore volume, and pore size distribution is now practiced routinely (1), and will not be treated in this study.

Surface composition and morphology for materials of catalytic interest have been extensively investigated over the last decade. The techniques that have been explored were originally designed to study the electronic properties of the surface and bulk of solids. They, in fact, represent some of the most useful contributions of surface science to the understanding of catalysis. They will be treated in Part 2, as part of the effect of impacting disciplines on catalysis.

The measurement of specific surface areas is a topic of active research in several laboratories, and has also seen considerable activity in the last decade. It is the primary subject of this section. The discussion emphasizes the status of surface characterization of various types of catalyst, and explores the impact of advances in this area on catalysis in general. Special consideration is given to those areas which may impact on the catalytic conversion of coal.

B. GENERAL DISCUSSION

Determination of the specific surface area of a catalyst involves techniques that can distinguish between the various components of the system. In the case of a supported catalyst, it involves a discrimination between the active catalyst material and the support. Techniques such as x-ray diffraction (2), transmission electron microscopy (3), and gas chemisorption have been used for this purpose.

Using x-ray diffraction techniques, the width of a line for a particular structure can be related to the crystallite size of aggregates of the compound. Thus, from line broadening, one can calculate the average particle size. The technique has two limitations, both of which become important at low catalyst loadings. One of these limitations is sensitivity. The support material usually interferes with the x-ray lines of interest, and this interference becomes severe at low concentrations. The other limitation is particle size. Particles below approximately 30-40 Å cannot be detected. This is a severe constraint since a large number of catalysts of interest have a considerable fraction of catalytic material that is smaller than this limit. For larger particles the procedure is routine.

The procedure for particle size determination by electron microscopy is also straightforward and routine. Complications are primarily related to sample preparation (to allow transmission) and resolution. The latter is in the 10 Å - 20 Å range, although even this resolution requires skillful operation and a sensitive instrument. Some problems are also encountered in obtaining truly representative data by normal procedures.

Because of the limitations of these techniques, the selective adsorption of gases has been the most common and effective means for the measurement of specific surface area. The technique relies on the difference between chemical and physical adsorption. Gases are used which selectively chemisorb on only one component of the catalyst. The technique will now be discussed in detail.

C. SURFACE AREA BY CHEMISORPTION

The use of gas adsorption for surface area determination of catalysts has been investigated primarily for metals. Other catalytic materials have received only limited attention. For this reason, metals characterization will be discussed separately, followed by a brief discussion of the more recent developments in the surface area measurement of oxides and sulfides.

1. METALS

As can be seen from Table IV-1, most of the metals of catalytic interest have been characterized by the selective adsorption of a number of gases. The subject has been reviewed recently (26), and therefore will only be discussed briefly in this section.

The most common sorbent is hydrogen. It is used extensively to determine the surface areas of Pt (13, 14), Ni (6-8), Co (6), Fe (4), Os, Ir, Rh, and Ru (25), Cu (6, 9), and, under special conditions, Pd (21). Its only drawback is the need for careful reduction of the surface and subsequent desorption of the reducing gas. To overcome this problem, Benson and Boudart (16) developed a technique whereby hydrogen is used to "titrate" oxygen atoms preadsorbed on the metal surface. As indicated by Dalla Betta (15), this procedure eliminates the complications of chemisorption, and also increases the sensitivity of the technique. The technique can be used for those metals that catalyze the H_2/O_2 reaction, which include Pt, Pd, Rh, and Ir. The "titration" of platinum has been studied most extensively (15-19), while the technique has been applied only recently to Pd (22) and Rh (24). Interpretation of the measurement on Rh is complicated by uncertainties in the stoichiometry of the hydrogen-rhodium surface species and evidence of partial bulk oxidation (24). The uncertainty in stoichiometry is not as great for the other metals. However, it is an important factor in the titration of Pt at high dispersions (small particle size). In this region, changes in the oxygen stoichiometry have been reported (18, 19). Chemisorption of H_2 is therefore still the most reliable procedure for highly dispersed catalysts. In the case of palladium, formation of a bulk hydride is avoided by operation

TABLE IV-1

SURFACE AREA MEASUREMENT OF METAL CATALYSTS

Metal	Chemisorbed Gas	Conditions	Reference
Fe	H_2	25°C, 100 Torr	4
	CO	25°C, 100 Torr	4
Co	H_2	25°C, 100 Torr	6
	CO	-195°C	5
Ni	H_2	25°C	6,7,8
	CO	25°C	7
Cu	H_2	25°C	6,9
	N_2O	90°C, 200 Torr	10
		25°C, 500 Torr	11
	CO	25°C, 100 Torr	6
Ru	H_2	25°C	23
	CO	25°C	20
Rh	H_2	25°C	24
	O_2	-80 to 300°C	24
	CO	25°C	24
	H_2/O_2	25°C	24
Pd	H_2	70°C, 1 Torr	21
	H_2/O_2	100°C, $P < 350$ Torr	22
	D_2/O_2	100°C, $P < 1000$ Torr	22
Ag	O_2	180°C, 10 Torr	12
	N_2O	150°C	12
Os	H_2	25°C	25
	CO	25°C	4
Ir	H_2	25°C	23
	CO	25°C	23
Pt	H_2	25°C	24
	CO	25°C	24
	H_2/O_2	25°C	24
	O_2	25°C	24

at higher temperatures (100°C) and the use of D_2 to avoid formation of the β-Pd-H phase (22).

Carbon monoxide is another gas used often in the measure of selective surface areas. In certain cases it is preferred over H_2. An example is Cu (6, 9) for which H_2 adsorption is slow. However, in all cases the primary limitation of the use of CO is its ability to adsorb in a linear and bridge mode, and to adsorption at ratios greater than 1:1 on small particles, thus leading to uncertainties about the correct stoichiometry (6, 20). Furthermore, considerable adsorption occurs on the support, thus requiring corrections that are often as high as the chemisorption on the metal in dilute systems.

Oxygen chemisorption has had only limited application, since many of the metals of interest form bulk oxides at room temperature or above. It has been used extensively, however, for the determination of the surface area of silver catalysts used in catalytic oxidation (12). In this particular case, the chemisorption is run at high temperatures (175-200°C) to minimize formation of the unstable silver oxide.

An alternate technique to measure surface area by oxygen chemisorption has been investigated recently (10-12). It involves using N_2O as an oxygen source, via the decomposition to N_2 and adsorbed oxygen. It has been used for measurement of the surface area of Cu (10, 11), as well as Ag (12). In the case of Cu, is is surprising that it does not lead to bulk oxidation, especially in view of the instability of the N_2O molecule relative to N_2 and atomic oxygen. The absence of bulk oxidation has been claimed below 100°C (10), an effect that is likely to be kinetic, as pointed out by the authors.

In summary, it is apparent that most metals of catalytic interest can be characterized by selective chemisorption, with some techniques more established than others. Hydrogen has been used most extensively, while CO and oxygen are used only in special cases. The situation is very different for oxides, as will be discussed next.

2. OXIDES

In sharp contrast to metals, the characterization of oxides by adsorption techniques has received only limited attention in the literature. The selectivity in gas chemisorption is much more limited, making the measurement procedures complex. The most common adsorbent that has been used in the past is CO. Dependence of the adsorption isotherm on sample preparation and pretreatment (reported, for example, for Co_3O_4/SiO_2 (27)) makes CO adsorption data often unreliable. However, few alternative techniques have been proposed.

One alternative to CO adsorption on oxides has been proposed by Shelef and co-workers. It involves NO chemisorption, and has been used to measure the surface area of oxides of iron (28), chromium (29), copper (30), and nickel (31). The technique relies on the observation that the adsorption of NO on a number of oxides follows a Freundlich-type isotherm. This behavior permits calculation of monolayer coverage by plotting the logarithm of the gas uptake against the logarithm of the equilibrium pressure at various temperatures. It is a promising technique for oxide characterization, and should be extended to other systems.

An oxide catalyst that is of great importance for coal conversion is cobalt molybdate supported on Al_2O_3. There have been very few attempts to characterize the selective surface area of this catalyst (32-34).

Most of the studies of gas adsorption have been directed at a study of the chemistry and kinetics of the interaction rather than a determination of surface area (35-38). In one recent attempt to relate gas adsorption to catalytic activity (32), the thermal desorption of hydrogen from $CoO-MoO_3-Al_2O_3$ catalysts was compared with thiophene hydrogenolysis activity. Of the various hydrogen bonding states observed, only the weakly bonded hydrogen showed a relationship to thiophene hydrogenolysis. It is unlikely, therefore, that hydrogen adsorption will become a routine technique for the characterization of this catalyst. Other gases, including H_2S and NO, should be explored.

D. SURFACE ACIDITY

In contrast to the determination of the specific surface area, the acidity of oxides has been studied extensively over the last two decades. Parameters that have been measured include acid strength, acid amount, acid type (Brønsted or Lewis), and acid distribution. Measurement techniques are routine and reproducible. They have been described in detail in a number of recent review articles (39-42), and will therefore not be discussed in this section. However, it should be stressed that surface acidity is an important aspect of the characterization of coal conversion catalysts, in particular for liquefaction and upgrading of coal liquids (43). It therefore has considerable importance in the development of catalytic coal conversion processes, and will be discussed in detail in Part 3 of this study.

E. IMPACT OF CHARACTERIZATION IN CATALYSIS

Any comparative study of the catalytic activity of materials is meaningless in the absence of specific surface area measurements. This was shown quite clearly in the study of Vannice (44), who re-examined the methanation activity of a number of transition metals. Prior activity data, which did not have the advantage of the surface area measurement techniques developed in the last decade, reported the following activity sequence (45): Ru > Ir > Rh > Ni > Co > Os > Pt > Fe > Pd. By contrast, Vannice found a different sequence when the rate data were corrected to unit surface area of the metal studied: Ru > Fe > Ni > Co > Rh $\sim$ Pd > Pt > Ir. The most dramatic difference was found for Fe, which was considered by the early workers to be a poor methanation catalyst. It reflects the difficulty in preparing iron catalysts of high surface area (46), and focuses attention on the real nature of the activity problem in this particular case: the need to find methods for stabilizing high surface area iron catalysts.

Many other examples of systematic comparisons of activity reported in the last decade rely on careful measurement of surface area. The extensive work of Sinfelt and collaborators on the hydrogenolysis and hydrogenation activity of transition metals is perhaps the most extensive study of this kind (25, 47). This work has helped to highlight the dramatic difference in the activity of metals for these two reactions, thus increasing the understanding of the behavior of these metals for many industrial processes.

In addition to these comparative studies, characterization has been responsible for the progress of several new ideas and concepts developed over the last decade. The areas discussed in Section III belong to this category. Determination of catalyst-support interactions, structural and chemical promotion, catalyst stabilization, and structure sensitivity would have been impossible in the absence of techniques for obtaining activity information on a per-unit area basis. This is true for the synthesis of new catalytic materials as well. As discussed in Section V, evaluation of new materials may be misleading in the absence of selective surface area information. For a long time, for example, it was believed that nickel boride was a more active hydrogenation catalyst than nickel and that chromia increased this activity considerably (48). Mears and Boudart, however, showed that on a Ni surface area basis, Ni_2B and Ni have the same activity (49). The effect of chromia was only a surface area effect: the activity per unit surface area of unpromoted and promoted nickel boride catalysts was constant over a seven-fold range of surface areas.

Elucidation of such surface area stabilization effects, and conversely, poisoning and sintering effects are an important aspect of coal conversion catalysis. It is therefore surprising that such limited attention has been given to the characterization of oxide catalysts, in particular in terms of selective surface area. In the case of HDS and HDN catalysts, this is a particularly important problem. To date, catalyst deactivation studies have been limited to studies of the changes in total surface area and pore volume distribution. Effects of selective poisoning, sintering, and possible chemical change of the active catalytic surface have not been investigated. Lack of catalyst characterization has also limited the understanding of the effect of promoters on the activity. As will be emphasized in Part 3, this is an area of catalytic coal conversion that requires more research.

F. REFERENCES

1. Gregg, S. J., and Sing, K. S. W., Adsorption, Surface Area and Porosity. Academic Press, New York, 1967.
2. Anderson, J. R., Structure of Metallic Catalysts, p. 364. Academic Press, New York, 1975.
3. Ibid., p. 363.
4. Sinfelt, J. H., and Yates, D. J. C., J. Catal. 10, 362 (1968).
5. Anderson, R. B., Hall, K. W., and Hofer, C., J. Amer. Chem. Soc. 70, 2465 (1948).
6. Sinfelt, J. H., Taylor, W. F., and Yates, D. J. C., J. Phys. Chem. 69, 95 (1965).
7. Brooks, C. S., and Christopher, G. L. M., J. Catal. 10, 211 (1968).
8. Yates, D. J. C., Taylor, W. F., and Sinfelt, J. H., J. Amer. Chem. Soc. 86, 2996 (1964).
9. Suzuki, M., and Smith, J., J. Catal. 21, 336 (1971).
10. Scholten, J. J. F., and Konvalinka, J. A., Trans. Faraday Soc. 65, 2465 (1969).
11. Osinga, Th. J., Linsen, B. G., and Van Beek, W. P., J. Catal. 7, 277 (1967).
12. Scholten, J., Knovolinka, J., and Beekman, F., J. Catal. 28, 209 (1973).
13. Vannice, M. A., Benson, J. E., and Boudart, M., J. Catal. 16, 348 (1970).
14. Hunt, C. E., J. Catal. 23, 93 (1971).
15. Dalla Betta, R. A., J. Catal. 31, 143 (1973).
16. Benson, J. E., and Boudart, M., J. Catal 4, 704 (1965).
17. Wilson, G., and Hall, K. W., J. Catal. 17, 190 (1970).
18. Wilson, G., and Hall, K. W., J. Catal. 24, 306 (1972).
19. Mears, D. E., and Hansford, R. C., J. Catal. 9, 125 (1967).

20. Dorling, T. A., and Moss, R. L., J. Catal. 7, 378 (1967).

21. Aben, P. C., J. Catal. 10, 224 (1968).

22. Benson, J. E., Hwang, H. S., and Boudart, M., J. Catal. 30, 146 (1973).

23. Sinfelt, J. H., and Yates, D. J. C., J. Catal. 8, 82 (1967).

24. Wanke, S. E., and Dougharty, N. A., J. Catal. 24, 367 (1972).

25. Dalla Betta, R. A., Cusumano, J. A., and Sinfelt, J. H., J. Catal. 19, 343 (1970).

26. Farrauto, R. J., "Determination and Applications of Catalytic Surface Area Measurements", presented at 77th National AIChE Meeting, Pittsburg, Pennsylvania, June 2-5, 1974.

27. Pope, D., Walker, D. S., Whalley, L, and Moss, R. L., J. Catal. 31, 335 (1973).

28. Otto, K., Shelef, M., J. Catal. 18, 184 (1970).

29. Otto, K., Shelef, M., J. Catal. 14, 226 (1969).

30. Gandhi, H., and Shelef, M., J. Catal. 28, 1 (1973).

31. Gandhi, H., and Shelef, M., J. Catal. 24, 241 (1972).

32. Kolosov, A. K., Shvets, V. A., and Kazanskii, V. P., Kinet. Katal. 16, 197-201 (1975).

33. Dollimore, D., Galwey, A., and Rickett, G., J. Chim. Phys. Phys.-Chem. Biol. 72, 1059 (1975).

34. Masoth, F. E., J. Catal. 36, 164 (1975).

35. Samuel, P., and Yeddanapalli, L. M., J. Appl. Chem. Biotechnol. 24, 777 (1974).

36. Aptekar, E. L., Bykhovskii, M. Ya, Krylov, O. V., Lebedev, Yu A., and Miroshnichewco, E. A., Kinet. Katal. 15, 1568 (1974).

37. Kawak, M., and Krajewski, J., Zesz. Nauk, Politech. Slask., Chem. 61, 11 (1973).

38. Slager, T. L., and Amberg, C. H., Can. J. Chem. 50, 3416 (1972).

39. Goldstein, M. S., in Experimental Methods in Catalytic Research (R. B. Anderson, Ed.), Chapt. 9. Academic Press, New York, 1968.

40. Tanabe, K., Solid Acids and Bases. Academic Press, New York, 1970.

41. Donnet, J. B., Bull. Soc. Chim. Fr., 3353 (1970).

42. Forni, L., Catal. Rev. 8, 65 (1973).

43. Boudart, M., Cusumano, J. A., and Levy, R. B., New Catalytic Materials for the Liquefaction of Coal, Report RP-415-1, Electric Power Research Institute, October 30, 1975.

44. Vannice, M. A., J. Catal. 37, 449 (1975).

45. Fischer, F., Tropsch, H., and Dilthey, P., Brennst.-Chem. 6, 265 (1925).

46. Boudart, M., Delbouville, A., Khammouma, S., and Topsøe, H., J. Catal. 37, 486 (1975).

47. Sinfelt, J. H., Catal. Rev. 3, 175 (1969).

48. Paul, R., Buisson, P., and Joseph, N., Ind. Eng. Chem. 44, 1006 (1952).

49. Mears, D. E., and Boudart, M., AIChE J. 12, 313 (1966).