FINAL REPORT DOE CONTRACT NO. DE-FG-93ER14358 (R. T. K. BAKER)

During the past three years a research project entitled "Carbon Deposition and Deactivation of Metallic Catalysts" has been supported by DOE, Basic Energy Sciences under grant number DE-FG02-93ER14358. The overall objective of this program has been to achieve conditions where it is possible to control the catalytic properties of a given metal by inducing perturbations to the reactive surfaces of the crystallites. One of the consequences of such an action is to enable one to alter the catalytic reactivity in such a manner so as to optimize the performance for a desired reaction pathway, while simultaneously suppressing the rate of detrimental side reactions, such as encapsulating forms of carbon deposition. Our strategy has centered around a study of the effect of introducing selected adatoms into the host metal and using the decomposition of ethylene to probe the manner by which the chemistry of the various faces of the crystallites is modified.

Specifically we have focused attention on the following scientific issues;

- The effect of selected metal adatoms on the carbon deposition characteristics of iron and cobalt during interaction with a hydrocarbon environment.
- The influence of selected non-metallic adatoms on the carbon formation activity of both these metals when treated in a hydrocarbon reactant.
- The relationship between the structural and morphological characteristics of the carbon deposits and that of the modified metal particles

1. *MODIFICATION OF THE CATALYTIC BEHAVIOR OF COBALT AND IRON BY THE INTRODUCTION OF SELECTED METAL ADATOMS*

The modification of the catalytic behavior of a metal by the addition of controlled amounts of other metals has been used extensively in order to alter both the activity and selectivity as well as to control the deactivation of active surfaces with respect to poisoning and deactivation due to carbon deposition. [1-5]. It is the understanding of this latter aspect that has eluded researchers in this area and presents challenges to the various mechanisms that have been proposed to account for carbon deposition on metal surfaces. McCarty and coworkers [6,7] used temperature programmed reaction techniques to establish the existence of several forms of carbon on deactivated nickel catalysts. From these studies graphitic overlayers and filamentous carbon growths were identified as being the most prevalent types associated with metals. The graphitic form of deposit tends to encapsulate the particle surface in contact with the reactant gas and thus normally results in rapid

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

deactivation of the catalyst. In contrast, filamentous carbon is produced by a process in which carbon diffuses through the particle and precipitates at the rear faces, thereby leaving the exposed faces free to undergo continued reaction. The net result of this behavior is that the catalyst system can accumulate large amounts of carbon and maintain activity for prolonged periods of time [8]. We have demonstrated that this condition can be achieved by the introduction of a small amount of selected adatoms, including copper, silver or tin, into the ferromagnetic metal. While the total amount of carbon deposited during reaction was increased significantly with the bimetallics, the growth process was such that it did not interfere with the desired reaction and as a consequence, catalytic activity of the particles was maintained for prolonged periods of time. It is apparent that when the bimetallic particles are undergoing reaction, distinct crystallographic faces are generated, some of which are capable of chemically dissociating ethylene, but they are unable to precipitate dissolved carbon atoms, and another set of faces that exhibit the reverse properties. A corollary of this phenomenon is that certain metal faces will be always free of solid carbon and therefore, available for continued decomposition of the hydrocarbon. The modification in the carbon depositing characteristics of the metal are rationalized according to the notion that the presence of the additive promotes surface atom reconstruction of particles and also induces electronic perturbations in the catalyst system.

Figure 1. Variation in the weight of solid carbon produced from the decomposition of ethylene after a period of 90 mins at 600°C as a function of the composition of a copper-cobalt catalyst.

Incorporation of as little as 1.0 to 2.0 % of either copper, silver or tin into the ferromagnetic metals causes a dramatic increase in the amount of carbon filaments produced during the decomposition of ethylene. Figures 1 and 2 show the influence of copper and silver on the carbon depositing characteristics resulting from the interaction of cobalt with ethylene and ethylene/hydrogen mixtures at 600°C. More importantly however, by careful control of the composition of the bimetallic it is possible to maintain catalyst activity for the hydrocarbon conversion to desired gas phase products almost indefinitely despite the accumulation of solid carbon. This aspect can be seen in Figure 3, where it is evident that while pure iron undergoes rapid deactivation when heated in an ethylene/hydrogen (1:4) mixture at 600°C, the addition of 10 to 30% copper to iron results in a dramatic enhancement in catalyst lifetime.

Figure 2. Variation in the weight of solid carbon produced from the decomposition of ethylene and ethylene/hydrogen (40:1) after a period of 90 mins at 600°C as a function of the composition of a silver-cobalt catalyst.

It is suggested that ethane is formed via hydrogenation of the olefin and originates from a condition where an ethylene molecule encounters two unperturbed ferromagnetic atoms and is adsorbed in a configuration where the C=C bond is oriented *parallel* to the surface. In the absence of an adatom such as copper, there will be a strong tendency for these adsorbed hydrocarbon species to link up with other similar entities and undergo polymerization and condensation to form a graphitic overlayer leading to catalyst

deactivation. When this same interaction takes place on a copper contaminated metal surface the fate of the adsorbed ethylene is quite different. Since copper does not chemisorb hydrocarbons, the pathway leading to encapsulation of the surface by graphite is blocked, and instead, hydrogenation to form ethane or scission of the C-C bond in the adsorbed molecule are the favored steps. On the other hand, when an olefin molecule comes into contact with a ferromagnetic metal atom whose nearest neighbor is a copper atom, then it is likely that the ethylene will bond to the surface in an *end-on* arrangement. In this conformation the adsorbed molecule may rapidly rearrange to form an ethylidyne intermediate, which will subsequently undergo C-C bond rupture to form methane. From analysis of both the amount of solid carbon deposited and the yield of gas-phase products in conjunction with a previously developed model [9] it is possible to obtain an estimate of the composition of the surface at which dissociative chemisorption of ethylene occurs under reaction conditions. An example of the total product distributions as a function of catalyst composition is presented for the copper-cobalt/ethylene system in Table 1. The values of $\{C_s + C_2H_6\}$ appear to provide one with an estimate of the percentage of cobalt atoms in the surface of the bimetallic particles when the ethylene decomposition has reached equilibrium. From these data it appears that the most active state of the catalyst is one containing approximately 80% of cobalt.

Figure 3. Amount of solid carbon formed from the decomposition of ethylene/hydrogen (1:4) at 600°C over various copper-iron catalysts as a function of reaction time.

TABLE 1. Effect of Catalyst Composition on the Product Distribution from the Decomposition of Ethylene after 90 min reaction at 600°C

% Co	% Cu	% Cs	% Ethane	% Ethylene	% Methane	% Ethane + Cs
0	100	0.0	0.0	0.0	0.0	0.0
25	75	39.2	11.0	47.7	2.2	50.2
50	50	67.3	10.7	17.4	4.6	78.0
75	25	70.2	12.4	10.1	7.3	82.6
90	10	72.0	10.0	10.8	7.2	82.0
95	5	69.6	9.0	14.6	6.8	78.6
98	2	60.2	7.4	29.1	3.3	67.6
100	0	3.6	3.6	91.8	1.0	7.2

2. *MODIFICATION IN THE CATALYTIC BEHAVIOR OF IRON AND COBALT RESULTING FROM THE INCORPORATION OF SELECTED NON-METAL ADATOMS*

It is now being recognized that the incorporation of controlled amounts of certain non-metallic atoms into metals, which have hitherto been regarded as poisons, can actually function as catalyst promoters. This approach is predicated on the assumption that the poison atoms are preferentially chemisorbed on sites that are active for undesirable reactions, while those sites which perform the desired reactions are preserved in an unadulterated state [10,11]. Previous work from this laboratory [12-14] has demonstrated that either pretreatment or continuous addition of 5 to 10 ppm H₂S to iron, nickel or cobalt undergoing reaction with ethylene had a significant impact on the catalytic activity of these metals, particularly with respect to the enhancement in yields of carbon filaments. *The data obtained from these studies was utilized by Union Carbide Chemicals and Plastics Company in an attempt to model the potential inhibiting effect of various volatile sulfides on carbon deposition phenomena encountered during steam cracking operations.* In the current program we have extended this investigation to cover the influence of chlorine on the same reactions.

Careful poisoning with chlorine has been found to be a very effective method of altering the activity and selectivity of catalysts and it has been suggested that such behavior could in part be attributable to induced electronic perturbations in the metal [15]. In catalytic reforming, the chlorine content derived from the metal precursor salt is thought to be directly related to the amount of carbon that accumulates on the catalyst [16]. As part of this task we conducted a series of experiments in which the conversion of ethylene to filamentous carbon was monitored during interaction with copper-cobalt bimetallics prepared from both nitrate and chloride precursors in an attempt to determine any possible

changes in the catalytic activity induced by the halide. When the reaction was conducted at 600°C no difference in the behavior of the two sources of cobalt with respect to either the amount or characteristics of the deposited solid carbon was detected. In a further set of experiments, the reaction temperature was lowered to 500°C and under these conditions the activity of the bimetallic derived from chloride precursors tended to increase as the reaction proceeded whereas the catalyst prepared from nitrates exhibited a steady decline in its ability to generate solid carbon. It is clear therefore, that the reaction temperature is one of the key factors in determining the effectiveness of a chlorine treatment on the metal catalyst. It would appear that at 600°C any residual chloride species are effectively desorbed and that the surfaces of the two bimetallic powders are essentially the same, both in composition and electronic character. On the other hand, at 500°C, there may still be significant desorption of the halogen, however, there is a sufficient residual concentration remaining at the surfaces of the copper-cobalt particles to have an impact on both the catalytic activity and the characteristics of the solid carbon structures [17].

In current studies, we are investigating the effect of small concentrations of chlorine on the carbon depositing characteristics of iron and cobalt when the halogen is introduced to the powdered catalyst system along with the reactant gas mixtures. Initial experiments indicate that when an ethylene/hydrogen mixture containing 25 ppm chlorine is passed over cobalt the maximum conversion of the olefin to solid carbon and gaseous products occurred at 400°C. It is significant that in the absence of chlorine no decomposition of ethylene was observed at this temperature. A similar pattern of behavior was found when iron was treated under the same conditions. In a further series of reactions the effect of chlorine concentration on the cobalt catalyzed decomposition of ethylene at 400°C was investigated. It was found that the optimum activity of the metal catalyst was achieved when 75 ppm of chlorine was present in the reactant gas stream. Although this work is still in progress it is clear from the data acquired thus far that the introduction of a critical amount of chlorine into the reactant gas can exert significant benefits on the performance of a metal catalyst.

3. *THE RELATIONSHIP BETWEEN MORPHOLOGY, CRYSTALLOGRAPHIC ORIENTATION OF THE METAL PARTICLES AND THE STRUCTURAL CHARACTERISTICS OF THE CARBON DEPOSITS*

Transmission electron microscopy examinations of samples of the solid carbon products showed that in the majority of experiments carried out in this project the major fraction of the deposit consisted of filamentous structures. Previous controlled atmosphere electron microscopy studies [18] have enabled us to identify the sequence of events leading to the formation of carbon filaments and the key steps in the growth process. When a hydrocarbon is adsorbed on a metal particle surface and conditions exist that favor the

scission of a carbon-carbon bond in the molecules, then the resulting atomic species may dissolve in the particle, diffuse to the rear faces and ultimately precipitate at the interface to form a filamentous carbon structure. The degree of crystalline perfection of the deposited filament is dictated by the chemical nature of the catalyst particle, the composition of the reactant gas and the temperature [19]. Surface science studies [20,21] have revealed that certain faces favor precipitation of carbon in the form of graphite whereas less ordered carbon will be deposited from other faces [22].

Depending on the crystallographic orientation of the faces that exist at the metal-carbon interface one can generate filaments that consist entirely of graphite platelets or contain a certain fraction of amorphous carbon, i.e. exhibit a duplex structure. Furthermore, the arrangement and spacing of the graphite platelets (d_{002}) is governed by the geometric orientation of the metal faces at which carbon precipitation occurs. By careful control of these variables we can manipulate, the crystallite arrangement, the interlayer spacing and the conformation of the filament structures. High-resolution transmission electron microscopy studies have revealed that the filaments consist of well-ordered graphite platelet structures, the arrangement of which can be tailored to a desired geometry by choice of the correct catalyst system. When the data from these examinations are combined with the information of the associated catalyst particle morphology, it is possible to develop models that describe many of the structural characteristics as well as some previously unknown mechanistic features of the various carbon filament conformations [23].

Three main types of crystalline arrangement of these structures can be identified, as illustrated in Figure 4. The associated catalyst particles can be seen as the dark shapes located within the filament structure. The carbon filaments possessing the "herring-bone" structure can be produced from the interaction of a copper-nickel catalyst with an ethylene/hydrogen at 600°C, Figure 4a. In this type of arrangement one can also encounter a step region. This form can be compared with that generated when a catalyst containing a large fraction of iron is reacted in the hydrocarbon environment. In this case, the graphite platelets are stacked in a direction parallel to the base of the particle and perpendicular to the fiber axis, Figure 4b. This arrangement is to be contrasted with that observed for a system in which supported iron particles are used as the catalyst and under these circumstances, graphite is precipitated from the lateral faces of the particle, and the platelets are aligned in a direction parallel to the fiber axis. The central region of carbon filaments formed from this system is generally hollow, and these structures may be regarded as "nano-ribbons", Figure 4c. Introduction of either sulfur or chlorine into the catalyst system produced major perturbations in the diffusion pathway of carbon and consequently in the morphological

characteristics of the carbon filaments. In these cases it was common to find the existence of regularly coiled structures.

It is these unique configurations that provide carbon filaments with a rare set of properties; a high electrical conductivity combined with a large fraction of active sites that correspond to the exposed edge regions of the graphite platelets that are available for interaction with various species. Because of the extraordinary combination of physical and chemical properties exhibited by these catalytically engineered carbon nanostructures, which are the result of the unique stacking and crystalline order present within the structure, there are tremendous opportunities to exploit the potential of this form of carbon in a number of areas. In many respects these highly graphitic filaments can be regarded as a new class of very fine molecular sieves [19].

Figure 4. Schematic representation of different types of carbon filament structures where the graphite platelets are arranged in (a) "herring-bone", (b) "perpendicular", and (c) "parallel" to the fiber axis.

MAJOR ACCOMPLISHMENTS

1. We have demonstrated that it is possible to modify the morphological characteristics of a metal particle in such a manner so as to generate two sets of faces; those that remain clean and available for continuous reaction with gas phase molecules regardless of the amount of solid carbon deposited and others that possess the ability to precipitate dissolved carbon atoms in the form of graphitic filaments.

2. Using the above concept we have been successful in developing procedures to suppress the formation of graphite overlayers on the faces of the particles where hydrocarbon conversions occur by forcing the carbon species to follow an alternative pathway leading to an enhancement in the growth of filamentous carbon. The ramifications of this behavior are that premature deactivation of the metal catalyst is avoided.
3. It has been established that the improvement in the performance of a given metal catalyst with respect to deactivation by solid carbon can be achieved by either the addition of small amounts of a second metal, such as copper, silver or tin, or by introducing a critical concentration of gaseous sulfur or chlorine into the hydrocarbon reactant stream.
4. While one might rationalize the modification in the catalytic action of a given metal in terms of a geometric effect when significant amounts of an adatom are present, it is difficult to conceive of how such an explanation can account for the dramatic enhancement in activity when only 1% of the additive is incorporated into the particles. It is possible that this change in behavior is attributable to electronic perturbations in the host metal lattice brought about by the presence of a foreign atom.
5. It is evident that by careful selection of the catalyst and reaction conditions, we have achieved a level of understanding where it is now possible to tailor the structural properties of carbon filaments. We believe that this type of material can have application in a variety of areas, including use as novel catalyst support media, electrodes in energy storage devices, gas separations and storage, and reinforcement of various matrices.

PUBLICATIONS FROM DOE BES GRANT DE-FG02-93ER14358

1. Effect of Sulfur on the Interaction of Nickel with Ethylene, W. T. Owens, N. M. Rodriguez and R. T. K. Baker, *Catal. Today* 21, 3 (1994).
2. A Review of the use of In-Situ Electron Microscopy Techniques for the Study of Iron-based Catalysts for Coal Conversion Processes. R. T. K. Baker and N. M. Rodriguez, *Energy and Fuels* 8, 330 (1994).
3. Influence of Sulfur on the Interaction of Iron with Carbon Monoxide. W. T. Owens, M. S. Kim, N. M. Rodriguez and R. T. K. Baker. "Catalyst Deactivation 1994" (B. Delmon and G. F. Froment, Eds.) *Studies in Surface Sci. and Catal.* Elsevier Science B. V., 88, 191 (1994).
4. Modification of the Catalytic Behavior of Cobalt by the Addition of Copper. A. Chambers, N. M. Rodriguez and R. T. K. Baker, *J. Phys. Chem.* 99, 10581 (1995).
5. Catalytic Engineering of Carbon Nanostructures. N. M. Rodriguez, A. Chambers and R. T. K. Baker, *Langmuir* 11, 3862 (1995).
6. A Review of In-Situ Electron Microscopy Studies of Metal/Metal Oxide-Graphite Interactions. R. T. K. Baker, *J. Adhesion* 52, 13 (1995).
7. In-Situ Electron Microscopy Studies of the Behavior of Metal Particles on Ceramic Substrates. R. T. K. Baker and N. M. Rodriguez in "Structure and Properties of Interfaces in Ceramics" *MRS Symposia Proc.* Vol 357 (1995).
8. Carbon Deposition on Iron-Nickel Alloy Particles, N. M. Rodriguez, M. S. Kim, F. Fortin, I. Mochida and R. T. K. Baker, *ACS Division of Petroleum Chemistry, Preprints* 40, 625 (1995).
9. Filamentous Carbon Formation from the Decomposition of Ethylene on Copper-Cobalt Bimetallics, A. Chambers, R. T. K. Baker and N. M. Rodriguez, *ACS Division of Petroleum Chemistry, Preprints* 40, 643 (1995).
10. The Modification of the Catalytic Activity of Iron by the Addition of Nickel, C. Park, R. T. K. Baker and N. M. Rodriguez, *ACS Division of Petroleum Chemistry, Preprints* 40, 646 (1995).
11. Influence of the Nature of the Catalyst Precursor on the Carbon Deposition Characteristics during Ethylene Decomposition over Copper-Cobalt. A. Chambers and R. T. K. Baker, *J. Catal.* 158, 356 (1996).
12. Influence of Copper on the Structural Characteristics of Carbon Nanofibers Produced from the Cobalt Catalyzed Decomposition of Ethylene. A. Chambers, N. M. Rodriguez and R. T. K. Baker, *J. Mater. Res.* 11, 430 (1996).
13. Effect of Copper on the Decomposition of Ethylene over an Iron Catalyst. N. Krishnankutty, N. M. Rodriguez and R. T. K. Baker, *J. Catal.* 158, 217 (1996).
14. Coking Problems Associated with Hydrocarbon Conversion Processes, R. T. K. Baker, *ACS Division of Fuel Chemistry, Preprints*, 41, 521 (1996).

15. The Influence of Silver Addition on the Catalytic Behavior of Cobalt. A. Chambers, N. M. Rodriguez and R. T. K. Baker, J. Phys. Chem. in press.
16. The Effect of Copper on the Structural Characteristics of Carbon Filaments Produced from Iron Catalyzed Decomposition of Ethylene, N. Krishnankutty, C. Park, N. M. Rodriguez and R. T. K. Baker, Catal. Today in press.
17. Carbon Deposition on Iron-Nickel Alloy Particles, N. M. Rodriguez, M. S. Kim, F. Fortin, I. Mochida and R. T. K. Baker, Appl. Catal. in press.
18. Carbon Deposition on Iron-Nickel during Interaction with CO/H₂ Mixtures, C. Park, N. M. Rodriguez and R. T. K. Baker, submitted to J. Catal.

REFERENCES

1. Sinfelt, J. H., *Accounts of Chem. Res.* 10, 15 (1977).
2. Sachtler, W. M. H., and van Santen, R. A., *Adv. Catal.* 26, 69 (1977).
3. Poncet, V., *Adv. Catal.* 32, 149 (1983).
4. Kelley, M. J., and Poncet, V., *Prog. Surf. Sci.* 11, 139 (1981).
5. Sinfelt, J. H., "Bimetallic Catalysts", an Exxon Monograph, John Wiley & Sons, New York, (1983).
6. McCarty, J. G., and Wise, H., *J. Catal.* 57, 406 (1979).
7. McCarty, J. G., Hou, P. Y., Sheridan, D. and Wise, H., in "Coke Formation on Metal Surfaces" ACS Symposium Series 202 (L. J. Albright and R. T. K. Baker eds.) Washington D.C. (1982) p. 253.
8. Rodriguez, N. M., Kim, M. S., and Baker, R. T. K., *J. Phys. Chem* 98, 13108 (1994).
9. Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* 131, 16 (1993).
10. Rostrup-Nielsen, J. R., in "Catalyst Deactivation" (C. H. Bartholomew and J. B. Butt Eds.) Elsevier Sci. Publ. Amsterdam, p.85 (1991).
11. Rostrup-Nielsen, J. R., *J. Catal.* 85, 31 (1984).
12. Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* 143, 449 (1993).
13. Owens, W. T., Rodriguez, N. M. and Baker, R. T. K., *Catal. Today*, 21, 3 (1994).
14. Owens, W. T., Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., in "Catalyst Deactivation 1994", (B. Delmon and G. F. Froment, Eds.) Elsevier Sci. Publ. Amsterdam, p.191 (1994).
15. Wu, X., Gerstein, B. C., and King, T. S., *J. Catal.* 135, 68 (1992).
16. Verderone, R. J., Pieck, C. L., Sad, M. R., and Parera, J. M., *Appl. Catal.* 21, 239 (1986).
17. Chambers, A., and Baker, R. T. K., *J. Catal.* 158, 356 (1996).
18. Baker, R. T. K., in "Carbon Fiber Filaments and Composites" Ed. by J.L. Figueiredo et.al. p.405, NATO ASI Series., Kluwer Academic Publishers, 1989.
19. Rodriguez, N. M., *J. Mater. Res.* 8, 3233 (1993).
20. Goodman, D. W., Kelley, R. D. Madey, T.E., and Yates, J.T., *J. Catal.* 63, 226 (1980).
21. Nakamura, J., Hirano, H., Xie. M., Matsuo, I., Yamada, T., and Tanaka, K., *Surf. Sci.* 222, L809 (1989)
22. Yang, R. T. and Chen, J. P., *J. Catal.* 115, 52 (1989).
23. Rodriguez, N. M., Chambers, A., and Baker, R. T. K., *Langmuir* 11, 3862 (1995).