Single crystals as model catalysts

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Recent work has demonstrated the special advantages of meshing in a single apparatus kinetic measurements at process-like conditions with modern surface analytical techniques for fundamental catalytic studies. These data have shown that low surface area monolithic materials can be used successfully to model certain catalytic systems. Virtually identical kinetic parameters have been found for the methanation reaction over single crystals of nickel and ruthenium as have been measured for high surface area nickel and ruthenium process catalysts. Surface probes have allowed the methanation reaction to be mechanistically dissected, in that the kinetics associated with the two major reaction steps have been individually measured. Using surface probes to monitor quantity and ordering of the impurity atoms, a correlation has been found between the electronegativity of the impurity atom and its catalytic poisoning ability. Electronic effects, as opposed to site blocking, are shown to dominate.

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I. INTRODUCTION

The areas of modern ultrahigh vacuum surface science and the surface science of heterogeneous catalysis have developed rather independently into their present forms. In the former case a wide array of surface spectroscopies have been employed to systematically study electronic structure and chemisorption primarily on well-defined systems, i.e., single crystals, and typically in an ultrahigh vacuum environment. In the latter case physical characterization and kinetic measurements have been the mainstays to define the high surface area materials customarily used. Correlations between these two areas have been made regarding electronic structure and chemisorption behavior; however, questions regarding these correlations invariably arise because of the nature of the materials and the large differences in the pressure regimes.

The recent applications of kinetic measurements over well-defined materials have begun to unify these two diverse areas of surface science. Combining the strengths of the ultrahigh vacuum surface probes with kinetic measurements has illustrated the potential wealth of information to be gained regarding the microscopics of heterogeneous catalysis.

In this paper we shall examine a reaction system which has been studied in perhaps more detail than any other as an example of the utility of model systems in addressing catalytic problems of major technological importance. This is the methanation reaction

\[ 3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O} \]

over single crystals of nickel and ruthenium. Much of this work has been reviewed\(^{1}\) in detail, therefore this account will merely focus on the highlights, particularly those best illustrating the unique capabilities obtained by integrating modern surface probes and kinetic measurements into a single apparatus.

II. EXPERIMENTAL METHODS

The specially built apparatus used in these studies\(^2\) is shown in Fig. 1. The surface analysis and preparation chamber is of the standard belljar type. The catalytic reactor, contiguous to the surface analysis system, is custom built and employs a retraction bellows supporting the catalyst. The sample can be translated to various positions as indicated. Typically the single crystals are spotwelded to short high-purity leads of similar material and heated resistively. High-purity gases, rigorously cleaned, are used to measure kinetics up to \(\approx 2\) atmospheres. Gas chromatography provides a

![Fig. 1. Ultrahigh vacuum apparatus for studying single crystal catalysts before and after operation at high pressure in catalytic reactor. Position 1. Crystal is in position for Auger electron spectroscopy study of surface composition, or of ultraviolet photoemission spectrum of surface species. Position 2. Crystal is in position for deposition of a known coverage of poisons on promoters for a study of their influence on the rate of a catalytic reaction. Position 3. Crystal is in position for a study of catalytic reaction rate at elevated pressures, up to 2 atm.](image-url)
convenient and sensitive technique for product analysis. Auger electron spectroscopy (AES) is used primarily to document the surface composition prior to and subsequent to reaction rate measurements.

III. RESULTS AND DISCUSSION

A. Reaction kinetics

A prerequisite to modeling “real” catalytic systems with single crystals is the ability to correlate essential kinetic parameters between the two systems. For nickel this has been done in rather dramatic fashion as shown in Fig. 2. The data shown for the single crystal rates represent steady-state, specific reaction rates, that is, the rates are normalized to the number of exposed metal atom sites. Also plotted in Fig. 2 are data acquired for nickel supported on alumina reported by Vannice. The agreement between the single crystal and supported catalyst is striking and clearly indicates the reaction to be “structure insensitive”. For this and other reactions insensitive to structural effects, the surface characteristics of the single crystal catalyst should mimic the surface characteristics of the active metal in a process catalyst in the same environment. The advantageous features of a single crystal are retained at no expense to the relevance of the measurements.

B. Reaction mechanism

Auger spectroscopic analysis of the active nickel catalyst following reaction is shown in Fig. 3. A carbonaceous species is present at a concentration equivalent to approximately 10% of a monolayer. Auger line-shape considerations indicate this carbon to be a “carbidic” form [see Fig. 4(d)]. This surface carbon can be produced in the absence of hydrogen by heating the crystal in pure CO. Following heating at 600 K, the carbon AES spectrum in Fig. 4(c) is observed. This spectrum corresponds to a “saturation” carbon coverage in that continued heating in CO results in no fur-
ther change in the carbon peak relative to the nickel peaks. Heating at higher temperatures results in a continuous increase in a "graphitic" carbonaceous species shown in Fig. 4(a). For comparison AES carbon data are shown for graphite and nickel carbide taken by Chang. 4 The "carbidic" carbon form can be removed by heating in high pressure hydrogen to produce methane. However, to unambiguously conclude that this surface carbon route is the major reaction pathway, kinetic measurements of both carbon formation and removal are required. The results 5 of these kinetic measurements are shown in Figs. 5 and 6. Several features of the carbon buildup results shown in Fig. 5 are noteworthy: (a) There are two carbon regions characterized by different Auger line shapes—a carbide region at ordinate values less than 0.28 and a graphite region for larger ordinates. Auger studies with low electron beam currents on a monolayer coverage of CO indicate that the saturation coverage at 600 K corresponds to approximately one-half monolayer. (b) The carbon signals are reproducible, well behaved, and depend on both reaction time and temperature. (c) The apparent saturation carbide level increases with temperatures between 500 and 700 K. (d) Entry into the graphite region occurs only after a certain level of carbide accumulates, and (e) entry into the graphite region is not possible on the time scale of these experiments for T<650 K. From these data the activation energy for carbide formation can be estimated to lie between 22 and 25 kcal mol\(^{-1}\). This is to be compared with the overall methanation activation energy of 24.7 kcal mol\(^{-1}\). More significantly the data at 450 K gives a turnover number for carbide formation of \(2 \times 10^{-9}\) compared to \(3 \times 10^{-4}\) for methane formation (see Fig. 2).

The reaction of surface carbide with hydrogen is shown in Fig. 6 at various reaction temperatures. The turnover number for carbide removal at 450 K is \(2 \times 10^{-4}\) compared to the carbide formation (\(2 \times 10^{-8}\)) and methane formation (\(3 \times 10^{-4}\)). From these data we conclude that at 450 K the rate for methane formation, carbide formation, and carbide hydrogenation are very nearly the same. Thus the reaction rate is determined by a delicate balance of the carbide formation and removal steps and neither of these is rate determining in the usual sense. Very similar data have been obtained for single crystals of ruthenium. 6

The interplay between the carbon formation and removal steps is illustrated by the set of experiments 2(b) shown in Fig.

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**Fig. 5.** The rate of carbon buildup on a Ni(100) catalyst by reaction with 24 Torr CO. Ordinate values for carbon have been normalized to the Ni\(_{333}\) Auger transition intensity.

**Fig. 6.** The rate of carbide removal by reaction with 100 Torr hydrogen. At each temperature shown, the Ni(100) surface was precarbided by exposure to 24 Torr CO at 600 K and then treated with hydrogen.

**Fig. 7.** Arrhenius plot of methane synthesis [N\(_{\text{CH}_4}\)] on a Ni(100) catalyst at total reactant pressures of 1, 10, and 120 Torr. H\(_2/\text{CO} = 4/1\).
7 in which the overall pressure of reactants is varied. Lowering the total pressure from 120 Torr has a dramatic effect on the rate of methanation. At 100 Torr a departure from Arrhenius linearity occurs at ~700 K. At 10 Torr a departure from Arrhenius linearity occurs at ~550 K at which temperature the rate of methane production begins to level. At 1 Torr the rate begins to turn over at a still lower temperature. This behavior is due to the relationship between temperature, pressure, and the surface hydrogen atom (H\textsubscript{ads}) concentration on the catalyst. At a given temperature, the concentration of H\textsubscript{ads} increases with increasing hydrogen pressure until saturation is achieved. Maximum hydrogenation of CO occurs at this saturation point which falls on the linear Arrhenius line. Further increase of pressure has little effect on the reaction rate. Concurrent with the drop in H\textsubscript{ads} concentration below saturation is an increase in the carbide level observed following reaction. In both cases of 10 and 1 Torr, the turning over of the rate has associated with it an increase in the carbide level following reaction. The surface concentration of H\textsubscript{ads} is critically controlling the carbon level as well as the methanation rate.

C. Catalyst poisoning by sulfur

An obvious extension of the previously discussed work is into surface modification by additives and their influence on reaction kinetics. Ultrathin vacuum techniques permit experiments to be carried out with a level of atomic characterization which is precluded using classical catalytic methods. Investigators\textsuperscript{6,9} using LEED, photoemission, and other techniques for investigation of the Ni(100)/sulfur system, agree that sulfur is chemisorbed with fourfold site coordination. The sulfur forms a p(2\times2) structure at one-quarter monolayer coverage and a c(2\times2) structure at one-half monolayer. The one-half monolayer corresponds to a saturation coverage. Figure 8 shows an Arrhenius plot for kinetic data obtained for the methanation reaction over a Ni(100) catalyst with varying amounts of preadsorbed sulfur. These sulfur levels were established by exposure of the sample to H\textsubscript{2}S at 300 K followed by a sample heating to 600 K. The surface coverage of sulfur was determined by monitoring the S\textsubscript{2p}/Ni\textsubscript{2p} Auger peak height ratio found for a saturated sulfur coverage.

For identical reaction conditions the sulfided surfaces show behavior remarkably similar to results for the clean surface at considerably reduced hydrogen partial pressure. For \(\theta_s = 0.04\), the reaction rate at 120 Torr departs from linearity at 600 K. For the clean surface a nearly identical plot was found at 10 Torr. For \(\theta_s = 0.04\) the surface carbon level begins to rise to the saturation level as the reaction begins to deviate from linear Arrhenius behavior. The response of the reaction rates to higher levels of sulfur is very similar. It should be noted that at temperatures <600 K, the reaction for the sulfided surface parallel that for the clean surface. This suggests that although the reaction rate is slowed, no fundamental change has occurred in the reaction mechanism.

It is clear from the results shown in Fig. 8 that the poisoning effect of sulfur is very nonlinear. Figure 9 shows this nonlinear relationship between the sulfur coverage and the methanation rate at 600 K. A precipitous drop is seen for the catalytic activity at the lower sulfur coverages. The poisoning effect quickly maximizes and no further reduction in reaction rate is found at sulfur levels exceeding 0.2 monolayers. Apparently sulfur bonded in the p(2\times2) configuration sufficiently deactivates the nickel surface for methanation that further addition of sulfur produces no perceptible

**FIG. 8.** An Arrhenius plot of the rate of methanation over a sulfided Ni(100) catalyst at 120 Torr and a \(H_2/CO\) ratio equal to four. Sulfur coverages (\(\theta_s\)'s) are expressed as fractional monolayers (1 cm\textsuperscript{2} Ni(100) equals 1.5 \times 10\textsuperscript{15} atoms).

**FIG. 9.** Methanation rate as a function of sulfur coverage on a Ni(100) catalyst. Pressure = 120 Torr, \(H_2/CO = 4/1\), reaction temperature = 600 K.
attenuation of the reaction rate. The unoccupied fourfold nickel sites remaining at a sulfur coverage of one-fourth monolayer are effectively poisoned both for carbon formation and carbon hydrogenation catalysis. The initial change in the reaction rate poisoning in Fig. 9 suggests that approximately ten equivalent nickel sites are deactivated by one sulfur atom. There are two possible causes for this effect: (a) a long-range electronic effect (ligand effect) or (b) an ensemble effect. Experimentally these two possibilities can be distinguished. If long-range electronic effects are most important, then the reaction rate should be expected to be a function of the relative electronegativity of the adatoms, all other things being constant. If indeed a ten nickel atom ensemble is required for methanation then changing the electronic character of the poison should have little effect on the reaction rate. Substituting phosphorus for sulfur in a similar set of experiments\textsuperscript{10} results in a marked change in the magnitude of poisoning at low coverages. Phosphorus, because of its less electronegative character, poisons only the four nearest neighbors metal atom sites. These results support the conclusion that long-range electronic effects are playing a major role in the deactivation process.

Chemisorption studies\textsuperscript{7,11,12} of H\textsubscript{2} and CO on a C, N, S, P, and Cl precovered Ni(100) surface support the conclusion drawn above. For both H\textsubscript{2} and CO chemisorption there is a correspondence between the relative electronegativity of the preadsorbed atom and the inhibition of sticking coefficients and the capacity of the surface for adsorption.

IV. CONCLUSIONS

By combining kinetic measurements with modern surface probes we have shown for the methanation reaction that:

1) The absolute rates measured for single crystals are in excellent agreement with values reported for high area supported catalysts.

2) AES analysis of an active catalyst indicates a low level of a "carbidic" carbon present on the surface.

3) Kinetic measurements of carbon formation from CO and subsequent removal in hydrogen are consistent with a mechanism which involves the hydrogenation of an active carbon species.

4) Poisoning of the methanation reaction over Ni(100) by sulfur is nonlinear with coverage— one sulfur atom deactivates approximately ten nickel atom sites. This, together with chemisorption data, is consistent with electronic effects playing a major role in the deactivation mechanism.

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\textsuperscript{2}A U.S. Department of Energy Facility


\textsuperscript{12}D. W. Goodman and M. Kiskanova, in preparation.
