A new method for model surface preparation of nickel/alumina catalysts, compatible with an ultrahigh vacuum environment, is described. The model system consists of a tungsten substrate, an evaporated aluminum film which is subsequently oxidized, and an evaporated, submonolayer coverage of nickel. This thin-film model has been used to study carbon monoxide methanation. The specific reaction rates and activation energy associated with this reaction compare favorably with the corresponding values found for high-area, supported nickel catalysts. Advantages and possible applications of the model system are discussed.

1. Introduction

Single crystals have been shown to accurately model certain heterogeneous catalytic systems [1]. For instance, Goodman and coworkers have [2–4] modeled nickel and ruthenium high-surface-area catalysts with Ni and Ru single crystals and found nearly identical kinetic parameters for CO methanation. Single crystals, which can be studied under process-like conditions, have the advantage of being ultrahigh vacuum (UHV) compatible and are thus suitable for characterization by a variety of surface spectroscopies and microscopies.

The obvious disadvantage of single crystals as model catalysts is the absence of metal–support intimacy. In the present study the model system has been modified, through the use of thin films, to include both the support and active metal. In practice we evaporate a thin film of nickel onto a previously prepared aluminum oxide film. This system provides UHV compatibility while retaining the support–metal contact of the process catalyst. The method of sample mounting and surface preparation is, to the authors’ knowledge, unique and will be described in some detail.
The reaction chosen for study is carbon monoxide methanation
\[ \text{CO} + 3 \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}. \] (1)
Studies of this reaction over high-surface-area supported nickel [5,6] and, more recently, single crystals of nickel [1-4] provide extensive kinetic data for comparison. The kinetic parameters measured for the thin-film model show excellent agreement with those found for single crystal and supported catalysts.

2. Experimental

The experimental apparatus, which was designed to combine high-pressure reaction and UHV surface studies, is similar to that described previously [2]. The vacuum system includes a cylindrical mirror analyzer with a coincident electron gun. Auger electron spectroscopy is used to characterize the model surface during sample preparation and before and after high pressure reaction. The large nickel (60 eV) and alumina (51 eV) transitions overlap and cannot be used conveniently for surface characterization. The nickel (848 eV) and alumina (35 eV) peaks were chosen instead because of ease of resolution. Sample translation out of the UHV chamber and into the adjacent catalytic reactor for high-pressure reactions is facilitated by a retraction bellows and straight-through valve. The sample head is commercially available with feedthroughs for temperature measurement and resistive sample heating. Surface temperature is measured by a tungsten–rhenium (26% and 5% Re) thermocouple spot-welded to the substrate. Gas chromatography with flame ionization detection is used for product analysis.

2.1. Substrate mounting

Tungsten foil was chosen as the substrate for the model surface because it can be resistively heated to temperatures in excess of 2000 K. A suitable

![Sample head and sample mounting configuration.](image)
method for mounting the sample was developed (fig. 1) using molybdenum leads slotted on one end to accept the tungsten sample (0.04 mm thick). The opposite ends of the leads were attached to the copper feedthroughs. A unique feature of this sample mount is a molybdenum–tungsten (heliarc) weld between the leads and the substrate.

Sample heating was enhanced by notching the sample into an “H” shape. The main body of the sample was 0.65 × 0.90 cm. The legs, which are the major source of electrical resistance, were 0.15 cm wide. It is critical that all legs be of equal length and width for uniform sample heating. This sample arrangement allows uniform heating to 1800 K.

2.2. Surface preparation

The tungsten substrate was cleaned by cyclic, low-pressure oxidation (1 × 10⁻⁶ Torr O₂) and high-pressure reduction (10 Torr H₂). Following oxidation/reduction, the surface consisted of only tungsten and oxygen, as determined by Auger spectroscopy (fig. 2a). Flashing to 1790 K did not decrease the surface oxygen coverage. Houston and Madey [7] reported that 2300 K is

![Fig. 2. Auger spectra showing steps in the preparation of the nickel/alumina model surface: (a) tungsten oxide surface after several repetitions of oxidation, reduction, and high-temperature flashes; (b) aluminum thin film deposited over tungsten oxide substrate (note the small oxygen signal from the tungsten oxide substrate); (c) surface following oxidation of aluminum thin film; (d) model surface following nickel evaporation onto aluminum oxide.](image-url)
required to completely remove all surface oxygen. Methane production over this tungsten oxide surface at 550 and 650 K was below the detectable level.

Aluminum and nickel evaporators were custom designed for the UHV chamber. The aluminum evaporator consisted of four strands of tungsten wire, 0.46 mm diameter, twisted and attached to copper feedthroughs. The tungsten strand was bent into a "V" shape and aluminum strips were wrapped around the point of the "V". Partial cuts of the strand were made on each side of the aluminum to localize heating. The nickel evaporator was designed similarly. The sample could be moved into or out of the line-of-sight of either evaporator during degassing or evaporation. Only one side of the substrate was coated and line of sight between the two evaporators was avoided. The sample was approximately 5 cm from either evaporator and the solid angle of evaporation encompassed the entire sample with little evaporation onto the molybdenum leads. The copper feedthroughs provided large heat sinks which maintained lead temperatures near ambient. Thus any nickel deposited on the leads should not appreciably contribute to the reaction products.

Aluminum was evaporated onto the room temperature sample after a 5 to 10 min degassing period. Auger spectra were recorded at 5 to 10 min intervals to determine the amount of Al deposited. The deposition process continued until the W(169 eV) signal disappeared (fig. 2b), indicating an aluminum depth greater than 5 Å [8].

The aluminum surface was oxidized in situ in 5 × 10^{-6} Torr O_2 at approximately 740 K. This process was repeated until no further oxide (510 eV) or alumina (51 eV) increase or Al(68 eV) decrease was observed. The resulting alumina surface was pure to the limits of Auger detectability (fig. 2c). Reaction at 550 K on the aluminum oxide showed negligible methane production.

Following oxygen removal from the system, the nickel evaporator was degassed for 5 to 10 min and the sample then flashed to 635 K to remove any adsorbed gases. Nickel was deposited at room temperature for 30 to 120 s with intermittent Auger checks to determine the amount of deposition. No elements other than Ni, Al, and O were detectable using Auger spectroscopy (fig. 2d). Sensitivity factors [9] were used to approximate the stoichiometry of the model surface of fig. 2d as Ni/Al_{1.6}O_{1.5}. This stoichiometry varied slightly from surface to surface because of changes in aluminum and nickel evaporation rates. No interdiffusion of the tungsten oxide substrate and the aluminum oxide was observed. Auger spectra taken at several positions on the surface showed similar Al: Ni ratios and therefore uniform nickel deposition.

2.3. Methanation

Carbon monoxide methanation was carried out in the reaction chamber after first retracting the sample and isolating the main chamber. Gas was transferred between the reaction chamber and GC via a manifold which was maintained at high vacuum when not in use.
Carbon monoxide was rigorously scrubbed in a liquid-nitrogen-cooled trap (glass wool) to remove nickel and iron carbonyls. The reaction chamber was filled with 24 Torr CO and 96 Torr H₂. A capacitance manometer was used for pressure measurement of reactant, product, and GC sample gases.

The sample was heated resistively at reaction temperatures (500 to 800 K) for 500 s. Reaction at room temperature was not detectable. Following reaction, the product gases were expanded through the gas manifold to the GC, the reaction chamber isolated from the GC and evacuated to high vacuum, and the sample returned to the main chamber for Auger analysis. Each model surface was used for one to three methanation studies depending on the degree of carbon and/or sulfur contamination. Contaminated samples were flashed to 1700 K to remove the nickel/alumina overlayer and a new model surface prepared.

3. Results and discussion

Fig. 3 is an Arrhenius plot for data from several separately prepared thin-film model catalysts, a nickel single crystal [1,2], and three alumina-supported catalysts [5,6]. For the model catalysts, Auger peak heights were used to
approximate the nickel coverage. Auger spectroscopy is roughly four times more sensitive to the Ni(848 eV) transition than the Al(35 eV) transition [9], due in part to the difference in electron escape depths at these energies (11 and 6 Å, respectively) [8]. The relative strengths of the nickel and aluminum signals indicated that the Ni deposition was less than three monolayers. The Al(35 eV)/Ni(848 eV) peak height ratio (average of ratio before and after reaction) was determined for each run. The average of these values was 1.0, indicating that less than a monolayer of nickel was deposited on the average sample. Turnover numbers were normalized to the model surface with the smallest average Al(35 eV)/Ni(848 eV) peak height ratio (0.31). This ratio was assumed to represent approximately one monolayer Ni coverage. The nickel thin-films were presumed to consist primarily of (111) planes, the most stable fcc facet; thus specific reaction rates were determined using the Ni(111) atom density of $1.88 \times 10^{15}$ atoms/cm$^2$ [4].

The magnitude of the turnover members at each reaction temperature for the thin-film model are close to those for the single crystal and supported systems. The activation energy for methanation, derived from the slope of the best-fit line through the model data is 17.7 kcal/mol, lower than the value of 24.7 kcal/mol reported for the Ni(100) single crystal [2]. However, the comparison between the measured specific rates for the three systems is remarkably good considering that these data are compiled from several different sample preparations. The scatter of the data presumably reflects the degree of precision in the model catalyst preparation. The Al/Ni ratio increased sharply after reaction for four of the five runs at temperatures greater than 600 K, suggesting agglomeration of the nickel (and hence less Al signal screening). Above 600 K nickel sintering, resulting in metal surface area reduction, could be responsible for the smaller apparent turnover numbers. This, in turn, would lead to the comparatively low overall activation energy associated with the model supported catalysts.

The ability to model heterogeneous catalytic systems with thin-films which retain the metal–support interaction opens new avenues for kinetic study in the area of UHV surface science. Traditional, high-surface-area supported catalysts are extremely difficult to study with electron microscopies and spectroscopies because of sample charging. This problem can, in principle, be eliminated with model thin-film catalysts as described in this work. Similarly, temperature-programmed desorption studies, which are difficult on powders, can be readily undertaken on thin-film models. These models have been shown here to reproduce kinetic parameters of the methanation reaction found for high-area supported catalysts. The results indicate suitability of these UHV compatible models as substitutes for the less tractable high-area systems.

A natural extension of the present work is to the study of other important catalytic reactions using similar model catalysts (e.g. Pt, Pd, and Ru over TiO$_2$ or SiO$_2$). These kinds of studies are currently in progress.
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References