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Activity of Tungsten as a Methanation Catalyst

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The catalytic activity of tungsten has been investigated for the methane synthesis from H_2 and CO. Starting with atomically clean tungsten, the activity for catalytic methanation rivals that of Ni, with tungsten being active at lower temperatures than Ni. These observations of high catalytic activity for tungsten suggest that the low activity seen in previous studies on tungsten catalysts may have been due to inadequate cleaning procedures.

INTRODUCTION

The development of sulfur-resistant catalysts to promote the methanation reaction is of importance because of the use of these catalysts in the production of synthetic natural gas from sulfur-bearing coals. There is evidence that Mo and W catalysts for methanation may possess a significant tolerance to sulfur since these catalysts are often sulfided before use. However, compared to the useful methanation catalysts such as Ni and Ru, both supported Mo and W catalysts are reported to exhibit low catalytic activity (*1*).

Recent studies of the mechanism of the methanation reaction on Ni have indicated that a form of surface carbon produced from CO disproportionation is easily hydrogenated to produce CH_4 (*2*, *3*). The involvement of surface carbon in the reaction suggests that those metals which severely weaken the CO bond (or, in the limit, cause dissociation of chemisorbed CO) might be good candidates for promoting the catalytic production of CH_4. Both tungsten and molybdenum fall into this category since it is thought that the strongly bound β-CO thermal desorption states originate, at least in part, from the recombination of adsorbed C and O species (*4*). All of the β-CO states on W undergo complete isotopic exchange in the reaction $^{12}C^{18}O + {}^{13}C^{16}O \rightarrow {}^{12}C^{16}O + {}^{13}C^{18}O$ (*5*).

The low catalytic activity reported for supported W and Mo catalysts may be due to the great difficulty in initially preparing these materials in a completely reduced and clean form. In the present work, we have determined that clean W prepared under ultrahigh vacuum conditions rivals Ni in its activity for the methanation reaction.

EXPERIMENTAL

Atomically clean W and Mo may be produced by heating the metals to 2400 K in an ultrahigh vacuum, a procedure commonly used in surface studies on these metals. We have developed an ultrahigh vacuum catalytic reactor in which it is possible to clean refractory metal filaments or ribbons in this fashion; following catalyst cleaning, a highly purified $CO + H_2$ mixture (19.6% CO) can be added at $\sim$100 Torr (1 Torr = 133.3 N/m^2), and the initially clean catalyst can be tested for catalytic activity using a continuous mass spectrometric sampling of the high-pressure mixture. It has been

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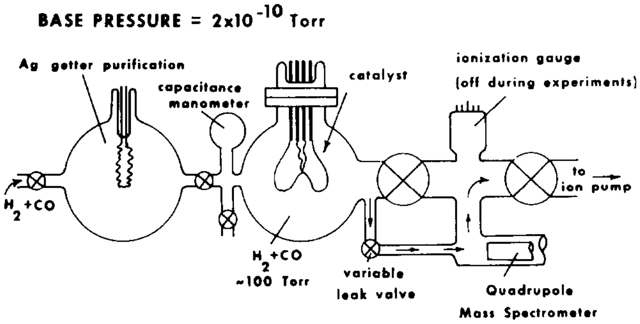

FIG. 1. Ultrahigh vacuum static catalytic reactor.

found that, for a Ni ribbon (10-cm^2 geometrical surface area), the turnover number [(number of CH_4 molecules produced per site·second)$_{T,P,x_{CO},x_{H_2}}$] measured is very similar to turnover numbers measured for high-area supported Ni catalysts (*6*, *7*), suggesting that on Ni the methanation reaction falls into the structure-insensitive category. The similarity between turnover numbers measured on high-area supported Ni catalysts and Ni ribbons indicates that valid kinetic measurements of catalytic activity may be made on surfaces of low area which are known to be atomically clean prior to reaction. Figure 1 shows a diagram of the apparatus. It is constructed mainly of glass with metal valves throughout and contains a W filament of 1.95-cm^2 geometrical area in the reactor bulb. The center temperature of the filament is monitored with a W/26% Re–W/3% Re thermocouple (0.0125 cm in diameter). The apparatus was processed by bake-out to achieve a base pressure of 2×10^{-10} Torr. An Ag getter film was evaporated on the walls of a gas storage vessel in ultrahigh vacuum, and the H_2–CO mixture was admitted and stored for at least 24 hr before use. Ag does not adsorb CO and is thought to be an excellent scavenger for S-bearing compounds. This is a precautionary purification procedure for the tank H_2–CO mixture (Matheson gas mixture).

The tungsten filament is cleaned by repeated heating in oxygen at 2×10^{-7} Torr, followed by flashing to 2425 K *in vacuo*; purified H_2–CO gas is then admitted to a pressure of 120 Torr, and the variable leak valve is adjusted to give a steady-state flow at 4.0×10^{-7} Torr past the quadrupole mass spectrometer. This continuous pumping contributes negligibly to pressure changes within the reactor during the run. The intensity of the mass 28 CO peak is monitored until it becomes constant with time; at this point the W filament was heated to the desired temperature, and the mass spectrum was measured at an electron ionizing energy of 70 eV. We employ the mass 15 peak to monitor the production of CH_4 since the parent mass 16 peak suffers interference with O^+ fragments from CO and H_2O.

RESULTS

Figure 2 shows the behavior of the mass 15 signal in the effluent gas, as a function of time, for various W catalyst temperatures. An induction period of ~5 min is consistently observed in all runs and is most probably related to the rate of diffusion of products through the reactant gas. The mass 15 signal then rises linearly with time. During later stages of reaction, the catalytic conversion rate decreases. The initial linear portion of each curve is used to estimate the initial rate of the reaction in the following fashion. First, the measured points are normalized to compensate for small gain changes which occur in the mass spectrometer from run to run. Second, we use the pressure change in the vessel to compute the absolute yield of CH_4 at a given time, since the reaction $3H_2 + CO \rightarrow CH_4 + H_2O$ involves a total loss of two molecules per CH_4 molecule produced. With these data, turnover numbers may be calculated for comparison with other data. We assume that the W geometrical area is the active catalytic area, and that there are 1.42×10^{15} W atoms/cm^2 [the surface density of the most closely packed W(110) plane].

Figure 3 shows the measured values of the specific rate of catalytic reaction as a function of the temperature of the W catalyst. It can be seen that the reaction begins at about 525 K, and that the reaction rate reaches a maximum value at ~675 K. That the observed tungsten activity is catalytic can be inferred from Figs. 2 and 3. The maximum turnover number from Fig. 3 is ~2.5, while, from Fig. 2, a typical reaction time is ~4000 sec. Thus, in these experiments, each tungsten surface atom has contributed to the formation of ~10^4 CH_4 molecules. For comparison, the turnover number for an Ni ribbon catalyst (*5*), as measured in the same apparatus at $T_{Ni} = 740$ K, is also indicated in Fig. 3. At temperatures below 740 K, the turnover number for the Ni ribbon catalyst decreased monotonically with decreasing temperature. Thus, over a wide range of temperatures, up to at least 740 K, the activity of tungsten greatly exceeds that of Ni for the methanation reaction at 120 Torr. In contrast to Ni, no CO_2 product is observed during the methanation reaction over W at any temperature studied. In addition, no C_2 or C_3 hydrocarbon products were observed.

During the course of the reaction at temperatures greater than 670 K (i.e., beyond the maximum in Fig. 3), the reflectivity of the W sample progressively decreased with time, and the deposition of a dark film was observed visually. The rate of deposition of the film increased with increasing temperature up to 850 K, the highest value at which measurements were made. At temperatures below the maximum, the sample remained highly reflective during the entire experiment (typically $\lesssim 2$ hr of heating in the gas mixture). The dark film could not be removed by subsequent heating in hydrogen, but was easily removed by heating in oxygen, with both carbon monoxide and carbon dioxide being produced. The deposit was apparently carbonaceous in origin. The rate of deposition of carbon may be in competition with the rate of methane production, leading to a fall-off in the initial rate of methane synthesis at high temperatures. A possible source of this carbon deposit is the disproportionation reaction of carbon monoxide ($2\ CO \rightarrow C + CO_2$) which has been observed with Ni (*2*, *3*) and Rh (*15*). To examine this possibility, the clean W surface was exposed to 24 Torr of CO with T_W = 400, 500, 600, 800, 900, 1200, and 1800 K. The gas phase was continuously sampled through the leak valve and was

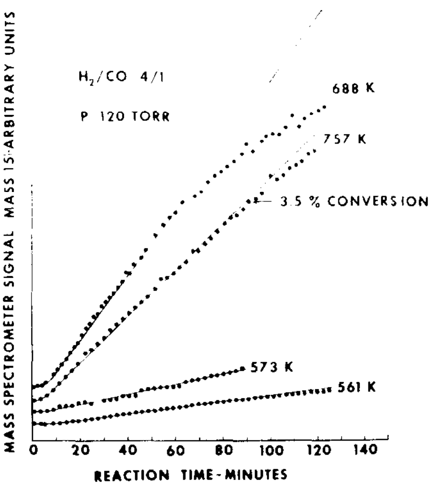

FIG. 2. Catalytic production of CH_4 on a tungsten filament as a function of time for various filament temperatures, with $H_2/CO = 4$ and $P_{total} = 120$ Torr.

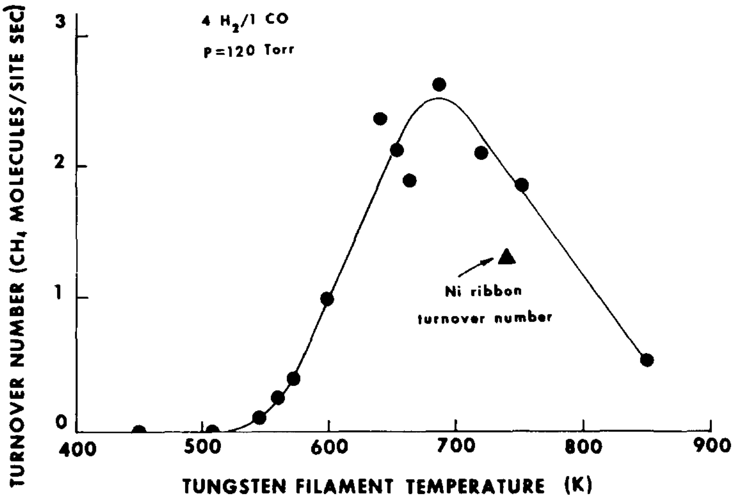

FIG. 3. Initial rate of CH_4 production on a tungsten filament as a function of filament temperature at $P_{total} = 120$ Torr and $H_2/CO = 4$.

analyzed with the quadrupole mass spectrometer. Mass 44 (CO_2) was monitored for 30 min at each temperature. Carbon dioxide was *not produced* at any temperature (the limit of detection is $CO_2/CO = 10^{-7}$), nor was there any evidence of a darkening of the W surface. This experiment indicates that the carbonaceous layer produced on the W surface which had been exposed to the $H_2 + CO$ mixture at temperatures above 670 K is not the result of the disproportionation reaction of carbon monoxide.

DISCUSSION

The observation of high catalytic activity for W in the methanation reaction appears, at first, to be quite surprising. It is almost axiomatic that W is a poor catalyst; it exhibits low catalytic activity for the methanation reaction (*1*). The catalytic activity of W for ethylene hydrogenation was reported to be anomalously low when compared with the activities of other metals in a correlation scheme involving percentage of *d* character (*8*). In contrast, however, W has been reported to be more active than many metals (including Ni) for a number of hydrocarbon + deuterium exchange reactions (*9*, *10*) on vacuum-evaporated metal films (including CH_4–D_2 exchange) (*11*).

The key to the activity of tungsten for the methane synthesis seems to lie in its surface preparation and the level of surface impurities. Powdered or supported W is difficult or impossible to clean by low-temperature (<1000 K) oxidation–reduction cycles (*12*). Even vacuum-evaporated films prepared under stringent conditions are often found to contain surface impurities (*13*). However, the surfaces of tungsten wires and ribbons can be prepared atomically clean in a reproducible fashion by high-temperature heating in an ultrahigh vacuum. In the present experiment, the use of ultrahigh vacuum surface-cleaning procedures and highly purified gases drastically reduced the possibility of surface contamination and permitted an accurate measure of the true activity of W as a methanation catalyst. In addition, W was found to be highly specific for CH_4 production: No C_2 or C_3 hydrocarbons were detected within the limits of sensitivity of the QMS (detection limit: $[C_2 + C_3]/CH_4 < 1\%$).

The production of CH_4 by W can be correlated with the thermal desorption behavior of CO on polycrystalline W (*14*). The temperature range of increasing CH_4 evolution (525–670 K) is above the range in which the molecularly adsorbed α-CO state desorbs rapidly. CH_4 production seems to precede the onset of desorption of the more strongly bound β_1-CO state. There is evidence for a continuum of chemisorbed CO states at low concentration between α- and β-CO desorption peaks (*14*) in the thermal desorption spectra. The catalytic formation of CH_4 coincides with this temperature region and may indicate that these states are involved in the reaction. At temperatures above 670 K, it appears that the rate of carbon deposition competes with the rate of CH_4 production. However, the rate of production of CH_4 is constant (linear portion of 757 K curve in Fig. 2), even under conditions in which a *visible* carbon deposit is forming on the catalyst surface. Either the reaction proceeds on sites at which carbon is not deposited, or a small fraction of the carbon itself must be capable of being hydrogenated. It is known that carbon deposited on Ni (*2*, *3*) or Rh (*15*) by the disproportionation of CO is in an "active" form and can be hydrogenated to methane. However, if an Ni surface containing the carbon is heated to 723 K, catalytically inactive graphitic carbon forms (*2*). The nature and indeed the source of the carbonaceous deposit formed on metal surfaces during catalytic methanation requires further study.

In closing it should be noted that previous investigations on tungsten surfaces have shown that CH_4 and CO_2 are produced upon desorption from a surface layer produced by formaldehyde adsorption (*16*). The CH_4 states desorb near 300 and 500 K, i.e., *below* the onset of catalytic CH_4 production from H_2 and CO seen in this work. The different temperature regimes and the fact that CO_2 is not a product of the $H_2 + CO$ reaction over tungsten suggest that species such as HCOH(ads) or HCO(ads) are not involved in the mechanism of CH_4 production from $H_2 + CO$ on tungsten surfaces.

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