Catalysis Letters 4 (1990) 173–180

THE EFFECT OF SULFUR ON THE DISSOCIATIVE ADSORPTION OF METHANE ON NICKEL

Xudong JIANG and D. Wayne GOODMAN

Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.

Received 14 September 1989; accepted 20 November 1989

Adsorption of methane on nickel, dissociative adsorption of methane.

The dissociative adsorption of methane was carried out on a Ni(100) surface covered with various amounts of sulfur under the high incident flux conditions of 1 Torr methane. Auger electron spectroscopy was used to measure the rate of carbon buildup and thus to determine the initial methane decomposition rates on the surface. It was shown that the sulfur atoms poison this reaction by a simple site-blocking process. These results are consistent with the activated dissociative adsorption of methane on Ni(100) occurring via a direct adsorption process.

1. Introduction

Activation of alkanes is an area of intense current research because this chemistry provides a promising route to convert an abundant natural resource into useful petrochemicals [1]. In general, alkane molecules are unreactive, because of the stability of C–C and C–H bonds. Methane is especially unreactive because of its unusually high C–H bond dissociation energy (104 kcal/mole) [2].

A number of recent studies on various metal surfaces have shown that alkane dissociation can be observed with molecular beam techniques [3–6] or at elevated pressures [7–8]. These results have shown the presence of a barrier along the dissociative reaction coordinate, and thus that alkane dissociation is an activated process.

In their molecular beam study of the activated dissociative chemisorption of CH_4 on Ni(111), Lee et al. have observed an exponential increase in the sticking coefficient (S_0) with increase in the normal component (E_n) of the incident molecule's translational energy. These workers have also observed the production of an adsorbed methyl species using high resolution electron energy loss spectroscopy [3–5]. These results were interpreted in terms of an adsorption process involving a highly deformed methane molecule. Lee and co-workers further speculated that the barrier to the dissociative chemisorption arose largely from the energy required to deform the CH_4 molecule sufficiently to allow a strong attractive interaction between the carbon and the nickel surface atoms. For the CH_4/Ni(100) system, Madix and co-workers found a 2 to 3.5 order of magnitude greater sticking coefficient at a given E_n than Lee et al. for the CH_4/Ni(111) system. In addition, Madix observed, in contrast to Lee et al. that S_0 scaled linearly, not exponentially, with E_n [6]. In these molecular beam studies, the dependence of the dissociation probability of alkanes on the translational energy was found to be essentially the same for different surface temperatures. It was concluded that the dissociative adsorption was a direct process, occurring during the initial collision of the alkane molecules with the surface rather than mediated by a precursor.

Stimulated by these molecular beam investigations, Beebe et al. measured the kinetics of the methane decomposition reaction on Ni(111), Ni(100), and Ni(110) single crystal surfaces under the high incident flux conditions of 1 Torr methane [7]. Their measured thermal sticking coefficients agreed very well with the molecular beam results on Ni(111) of Lee et al. [3] but compared poorly with the results on Ni(100) of Madix and co-workers [6]. Sault and Goodman extended Beebe et al.'s work to higher alkanes by investigating the dissociative adsorption of ethane, propane, and n-butane on Ni(100) at high pressures [8]. They compared their results with the results of the molecular beam study of alkane dissociation on Ni(100) and attributed the discrepancy to the behavior of alkane molecules with very low normal kinetic energies which have sticking probabilities below the limits of detection of the beam experiment. It was proposed that the dissociation of alkanes larger than methane occurs via a trapped molecular precursor. A molecular precursor state has also been postulated for the adsorption of methane by W(100) and W(111) [9,10]. According to the precursor model of chemisorption, the gas molecules first populate a weakly adsorbed molecular state known as a precursor state and then either chemisorb, or desorb into the gas phase [11].

As part of our continuing efforts to acquire a better understanding regarding the mechanism of methane activation as well as the effects of surface chemical modifiers, we present here the results of the dissociative adsorption of methane on a Ni(100) surface pre-adsorbed with varying coverages of sulfur under the high incident flux conditions of 1 Torr methane.

2. Experimental

Experiments in this study were performed in an apparatus similar to the one described in detail previously [12]. Briefly, it consists of a main analysis chamber and a contiguous high-pressure reaction chamber, both of which are of UHV construction. The main analysis chamber is equipped with a single pass cylindrical mirror analyzer with an integral electron gun for Auger electron spectroscopy, a quadrupole mass spectrometer for residual gas analysis, a titanium sublimation pump and an ion pump. The high-pressure reaction chamber is pumped by a turbo-molecular pump and separated from the analysis chamber by an all-metal gate valve. A strainless steel bellows assembly allows the sample to be transferred between these two chambers. The base pressure of the system is typically 1×10^{-10} Torr.

The high purity (99.995%) nickel single crystal rod, supplied by Aremco Products, Inc., was oriented using Laue back diffraction and spark-cut to within 0.5° of the desired (100) crystal plane. It was then polished through a series of emery papers, diamond paste, and 0.05 μ alumina slush until a mirror finish was obtained. A high purity tantalum wire (0.020″) was spot-welded to the periphery of the crystal for resistive heating. A pair of chromel-alumel thermocouple wires spot-welded to the edge of the crystal were used to monitor the temperature of the crystal.

Research grade methane with a minimum purity of 99.99% (Matheson Gas Products, Inc.) was used in this study. Before admission into the reaction chamber, the methane was further purified by storage in a liquid nitrogen-cooled zeolite-filled trap to eliminate CO and hydrocarbon impurities. Research grade oxygen and hydrogen, supplied by Matheson Gas Products, Inc., and CP grade hydrogen sulfide, supplied by Air Products & Chemicals, Inc., were used as received.

The crystal cleaning procedure consisted of oxidation in 1×10^{-8} Torr oxygen at 1473 K for 10 minutes and reduction in 1 Torr hydrogen at 830 K for 25 minutes. A capillary doser was used to direct the oxygen to the crystal surface so that the local pressure near the crystal during oxidation was approximately twenty times higher than the background pressure. This oxidation treatment at high temperature was necessary and efficient to thoroughly eliminate sulfur and carbon from the near surface region.

The same experimental procedures outlined in ref. [7] were used in this study. After admission of methane to the reaction chamber with the sample temperature below 350 K, the crystal was quickly heated to reaction temperature $T_{\text{reaction}} \pm 2$ K and held at this temperature for the desired reaction time, e.g., 15 seconds. The heating was then turned off and reaction mixture pumped away. With the crystal temperature held at 550 K, the gate valve was opened, and the crystal lowered to the Auger position. Although the surface composition did not fluctuate significantly across the crystal surface, care was exercised to reproduce the crystal position each time an Auger spectrum was acquired.

The sulfur was deposited onto the crystal surface by exposing the crystal to hydrogen sulfide at room temperature and then heating to 600 K [13]. It has been shown that on Ni(100) the sulfur atoms occupy four-fold hollow sites, forming a $p(2 \times 2)$ structure at one-quarter monolayer coverage and a $c(2 \times 2)$ structure at one-half monolayer, which corresponds to a saturation coverage [14–16]. (One monolayer, ML, is defined as one sulfur atom per surface nickel atom.) Previous studies have established that at saturation sulfur coverage the Auger ratio S (152 eV)/Ni(848 eV) = 2.4 [17]. This S/Ni Auger value was used to calibrate the sulfur coverage in this study.

After reaction, the Auger ratio C (272 eV)/Ni (848 eV) was measured and assumed to be proportional to the concentration of carbon atoms present on the nickel surface [18,19]. Previous studies have shown that on Ni(100) surfaces the saturation carbon coverage represents approximately 0.5 ML with a corresponding Auger ratio C (272 eV)/Ni (848 eV) = 0.28 [20]. This ratio was used to calculate the initial reaction rates expressed as methane decomposition events per site, per second.

After reaction at one temperature, the crystal was flashed to 1100 K causing the carbon deposited on the surface by dissociation of methane to diffuse into the bulk [8]. After several reaction cycles, the oxidation and reduction cleaning procedure described above was employed again to deplete the carbon in the near surface region. Various blank experiments outlined in ref. [7] were carried out periodically to ensure that no spurious surface carbon contamination was operative.

3. Results and discussion

Figure 1 shows the carbon buildup on a Ni(100) surface with less than 0.01 ML sulfur after reaction with 1.00 Torr of CH_4 at various temperatures for several reaction times. These results are identical within experimental error to the results on a clean Ni(100) surface [7]. The finite interval required to bring the sample to the reaction temperature was taken into account as follows: The plots of the C/Ni Auger ratios as a function of reaction time were extrapolated to a common point of zero carbon coverage and this point designated as the zero point of the "effective reaction time". In all of the Auger spectra obtained in this study, the C

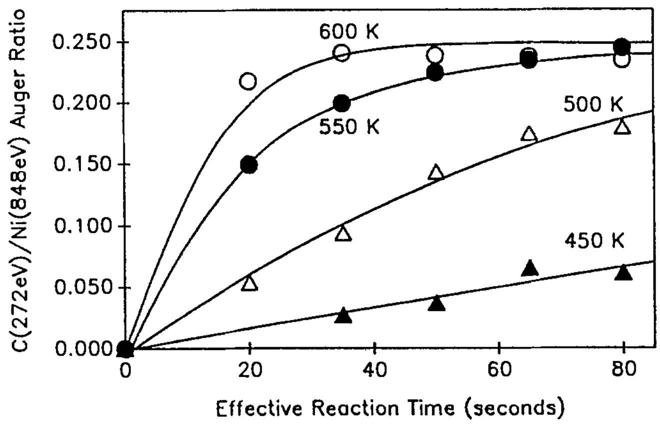

Fig. 1. The carbon buildup on Ni(100) surface with 0.008 ML sulfur as a function of the temperature and effective reaction time. $P_{\text{methane}} = 1.00$ Torr.

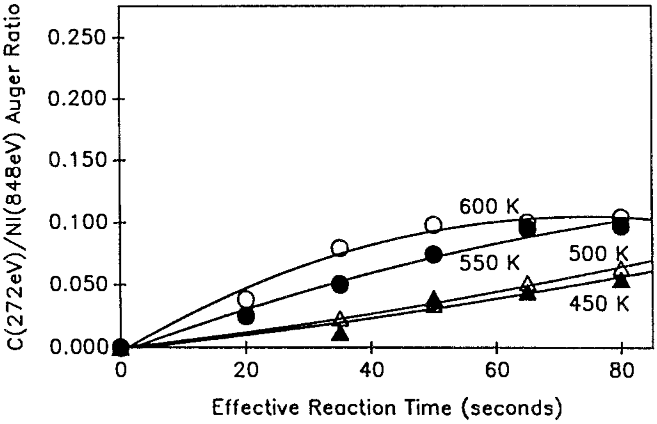

Fig. 2. The carbon buildup on Ni(100) surface with 0.202 ML sulfur as a function of the temperature and effective reaction time. $P_{\mathrm{methane}} = 1.00$ Torr.

(272 eV) peak was typically a carbidic carbon lineshape which did not change with coverage.

A direct correlation is evident between the coverage of sulfur and the rate of dissociative adsorption of methane at fixed reaction conditions. As shown in fig. 2, for a sulfur coverage of 0.2 ML, a significant attenuation is observed in the initial rate and the apparent saturation coverage of the product carbon. From the slope at the origin of the plots in figs. 1 and 2, and similar figures for a range of sulfur coverages, the initial methane decomposition rate on Ni(100) with different sulfur coverages can be calculated at various temperatures. Figure 3 shows that

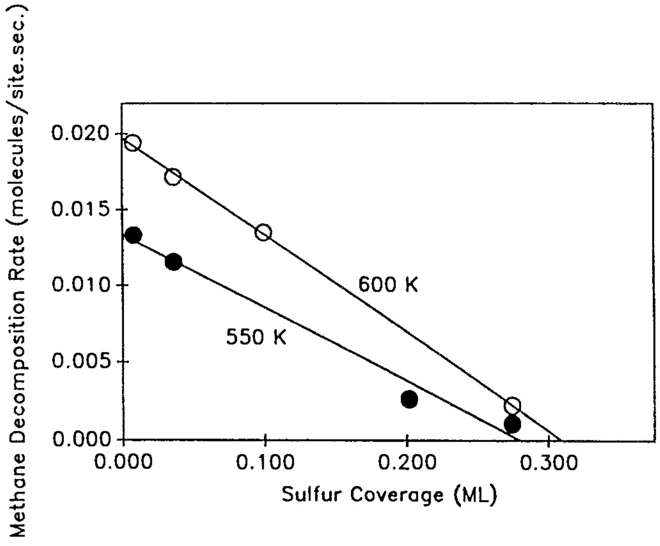

Fig. 3. The initial methane decomposition rate on Ni(100) surface as a function of the sulfur coverage. $P_{\mathrm{methane}} = 1.00$ Torr.

the initial methane decomposition rate decreases linearly with sulfur coverage and drops to zero at a sulfur coverage of ~ 0.3 ML.

The data of fig. 3 are fit by a simple first-order Langmurian form

$$S(\theta_s) = S_0(1 - \alpha\theta_s)$$

where $S(\theta_s)$ is the sticking probability of methane at a given sulfur coverage, θ_s; S_0, the clean surface methane sticking probability; and α, a parameter which corresponds to the number of "dissociation sites" that each sulfur atom blocks. The data here yield a value of $\alpha = 3$ implying that each sulfur atom on the surface blocks three "dissociation sites" for methane activation.

The Langmurian form of the methane dissociative adsorption kinetics as a function of sulfur coverage indicates that an extrinsic precursor is not involved in the activation of methane on a sulfur covered Ni(100) surface. Furthermore, these results are consistent with a relatively small number of sites (~ 3) being required for methane dissociative adsorption. This is in conflict with previous work by Frennet and coworkers [21] who have suggested that a considerably larger number of sites (~ 7) is required for the activation of methane on rhodium. On the other hand, the results here are in complete agreement with recent work of Hamza and Madix [6] who, using molecular beam techniques, have determined that methane activation on a carbon covered Ni(100) surface requires three atom sites.

Arrhenius plots for the dissociative adsorption of methane as a function of sulfur coverage yield activation energies of 6.5 ± 2.4 kcal/mole, approximately the same as the previously determined for clean Ni(100) [7]. These results, likewise, are consistent with a dissociation mechanism involving a direct process. That is, the effects of sulfur are entirely local or steric. The dissociation process is blocked effectively for those sites bonded directly to the sulfur but virtually unaffected at the sites that are not directly obstructed by the sulfur.

It is instructive to compare the effect of sulfur on the dissociative adsorption of methane in this study with the effects of sulfur on the chemisorption and reaction of other adsorbates. Previous studies have shown that for methanation reaction over Ni(100), the poisoning effect of the sulfur was very nonlinear, with ten or more equivalent nickel sites being deactivated by one sulfur atom [22,23]. From these results it was concluded that "long-range," (next-nearest neighbor) electronic effects were playing a significant role in the sulfur deactivation of a nickel methanation catalyst. Similarly, for the reaction of cyclopropane with hydrogen over Ni(100), the addition of sulfur led to a significant reduction in carbon-carbon bond-breaking ability of the nickel surface [24].

The absence of any apparent "long-range" effects in the poisoning by sulfur of the dissociative adsorption of methane on nickel adds further support to a mechanism in which methane molecules dissociatively adsorb on Ni(100) through a direct process. In a direct process, as the distance between the methane molecules and the surface becomes smaller than the equilibrium distance for molecular adsorption, a repulsive barrier is encountered. Translational and vibrational energy is required to overcome this repulsive force with a concomitant deformation of the methane molecule, for example, from T_d to C_{3V} symmetry. The carbon atom in the methane molecule approaches close enough to the nickel surface atom such that the metal-carbon interaction becomes strongly attractive. Dissociation follows, involving the breaking of a C-H bond and the formation of a Ni-C and Ni-H bond. In the Boltzmann gas surrounding the crystal, only a small portion of the methane molecules has the required translational and vibrational energy to undergo this dissociative adsorption process.

Dosing Ni(100) with sulfur leads to the sulfur atoms occupying four-fold hollow sites. Recent LEED, HREELS, and SEXAFS studies of ordered sulfur overlayer on Ni(100) have shown that sulfur sits approximately 1.4 Å above the surface in a $c(2 \times 2)$ structure [25,26]. Considering that the interatomic distance in nickel is 2.492 Å [27], and that one adsorbed CH_4 molecule occupies an area of 18.1 $Å^2$ [9], the presence of sulfur atoms will prevent methane molecules that strike the four nearest neighbor nickel atoms from getting close enough to the surface nickel atoms to dissociate.

In summary, methane dissociative adsorption on Ni(100) surface pre-adsorbed with sulfur under the high incident flux conditions of 1 Torr methane indicates that sulfur atoms poison this reaction by a simple site blocking mechanism. These results are consistent with a mechanism for the activated dissociative adsorption of methane on Ni(100) involving a direct rather than a precursor mediated process.

Acknowledgments

We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

References

[1] R.G. Bergman, Science 223 (1984) 902.

[2] S.W. Benson, *Thermochemical Kinetics*, 2nd ed. (Wiley, New York, 1976) p. 309.

[3] M.B. Lee, Q.Y. Yang, S.L. Tang and S.T. Ceyer, J. Chem. Phys. 85 (1986) 1693.

[4] S.T. Ceyer, J.D. Beckerle, M.B. Lee, S.L. Tang, Q.Y. Yang and M.A. Hines, J. Vac. Sci. Technol. A 5 (1987) 501.

[5] M.B. Lee, Q.Y. Yang and S.T. Ceyer, J. Chem. Phys. 87 (1987) 2724.

[6] A.V. Hamza and R.J. Madix, Surface Sci. 179 (1987) 25.

[7] T.P. Beebe, Jr., D.W. Goodman, B.D. Kay and J.T. Yates, Jr., J. Chem. Phys. 87 (1987) 2305.

[8] A.G. Sault and D.W. Goodman, J. Chem. Phys. 88 (1988) 7232.

[9] J.T. Yates, Jr. and T.E. Madey, Surface Sci. 28 (1971) 437.

[10] J.T. Yates, Jr. and T.E. Madey, J. Vac. Sci. Technol. 9 (1972) 672.

[11] R.P.H. Gasser, *An Introduction to Chemisorption and Catalysis by Metals* (Clarendon, Oxford, 1985).
[12] D.W. Goodman, R.D. Kelley, T.E. Madey and J.T. Yates, Jr., J. Catal. 63 (1980) 226.
[13] D.W. Goodman, J. Vac. Sci. Technol. 20 (1982) 522.
[14] H.D. Hagstrum and G.E. Becker, Phys. Rev. Letters 22 (1969) 1054.
[15] H.D. Hagstrum and G.E. Becker, J. Chem. Phys. 54 (1971) 1015.
[16] G.B. Fisher, Surface Sci. 62 (1977) 31.
[17] M. Kiskinova and D.W. Goodman, Surface Sci. 108 (1981) 64.
[18] F.C. Schouten, E.W. Kaleveld and G.A. Bootsma, Surface Sci. 63 (1977) 460.
[19] F.C. Schouten, O.L.J. Gijzeman and G.A. Bootsma, Surface Sci. 87 (1979) 1.
[20] D.W. Goodman, R.D. Kelley, T.E. Madey and J.M. White, J. Catal. 64 (1980) 479.
[21] A. Frennet, G. Lienard, A. Crucq and L. Degols, Surface Sci. 80 (1979) 412.
[22] D.W. Goodman and M. Kiskinova, Surface Sci. 105 (1981) L265.
[23] D.W. Goodman, Acc. Chem. Res. 17 (1984) 194.
[24] D.W. Goodman, J. Vac. Sci. Technol. A 2 (1984) 873.
[25] S. Brennan, J. Stöhr and R. Jaeger, Phys. Rev. B 24 (1981) 4871.
[26] S. Lehwald, M. Rocca, H. Ibach and T.S. Rahman, J. Electron Spectrosc. Rel. Phenom. 38 (1986) 29.
[27] W.B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2 (Pergamon, New York, 1967).