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Methane activation on clean and oxidized Ni(100)

Robert A. Campbell, János Szanyi, Petra Lenz and D. Wayne Goodman [1]

Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA

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The activation of methane was investigated on a clean and oxidized Ni(100) surface in the pressure range of 0.05–1.0 Torr. The results are most consistent with a precursor mediated mechanism being primarily responsible for the reactive sticking of methane on the clean Ni(100) surface. This contrasts with the Ni(111) surface where dissociative adsorption has been determined to occur predominantly through the direct mechanism. The reaction probability of methane on the NiO films was significantly lower than that observed for the clean Ni(100) surface and exhibited an apparent activation energy of 8.8 ± 1.1 kcal/mol. The results suggest that methane activation on NiO occurs on defect metallic nickel sites.

Keywords: Methane activation; thin film nickel oxide; Ni(100)

1. Introduction

The conversion of methane to higher hydrocarbons is a very attractive way to utilize this abundant energy resource. However, the relatively high stability of methane makes its activation a challenging technological problem. Research related to the activation of methane in the last decade has addressed the development of efficient catalysts and reaction conditions [1,2] and/or the nature of the dissociative adsorption of methane with active catalytic surfaces. The study of the reaction of methane with Ni single-crystal surfaces and model thin films of NiO is a key step in understanding the catalytic chemistry of methane on these materials.

Previously, the activation of methane has been studied on the Ni(111) [3–9], Ni(110) [4,10], and Ni(100) [3,4,11–13] surfaces by means of high incident flux "bulb" experiments, molecular beam techniques and theoretical calculations. The initial sticking probability of methane in the bulb experiments has been observed to be highest for the Ni(110) surface followed by the Ni(100) and

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[#1] To whom correspondence should be addressed.

Ni(111) surfaces [4]. This order of activity follows the trend in which the more open surface is the most active and the closed packed surface is the least active. Activation energies were found to be ≈ 13 kcal/mol for the Ni(111) and Ni(110) surfaces and ≈ 6.5 kcal/mol for the Ni(100) surface [4].

In the last several years experiments have addressed the detailed dynamics of the methane reactive sticking process [4,5]. For example, for the Ni(111) surface, molecular beam and bulb experiments have been carried out and the results compared [4,5]. From this comparison the conclusion was drawn that direct dissociative chemisorption rather than a precursor mediated mechanism was operative for methane activation on Ni(111). Specifically in the bulb experiments the rate of methane reactive sticking was monitored as a function of pressure for a constant methane exposure at 600 K [5]. No reactive sticking of methane was observed at pressures less than 0.2 Torr; however, raising the pressure to 1.0 Torr resulted in significant methane activation. These results are consistent with a direct activation process being operative in that, as the pressure of the methane is increased above 1.0 Torr, the inelastic mean free path of the methane molecules is significantly decreased. Accordingly at ≈ 1.0 Torr a boundary layer of methane exists at the Ni(111)–methane interface whose temperature is completely equilibrated with the Ni(111) surface. An increase in the methane temperature leads to a corresponding increase in the fraction of methane molecules in the high energy tail of the Boltzmann distribution. It is precisely these molecules which have been shown via molecular beam studies to have higher sticking probabilities [6]. On the other hand, at pressures < 0.2 Torr the methane gas is essentially at room temperature, independent of the surface temperature, and the fraction of methane molecules in the high energy tail is correspondingly lower. By maintaining the overall number of collisions constant the inefficiency of "cold" methane for reactive sticking compared to "hot" methane clearly indicates that the dissociative reaction of methane on the Ni(111) surface is dominated by the direct mechanism [5]. Unfortunately, similar experiments have not been carried out for the Ni(100) surface. Results for this surface are critical since the Ni(100) surface is significantly more active toward methane dissociation than is the Ni(111) surface [4].

The growth and reactivity of model thin films of NiO grown on a Ni(100) surface have been studied by Hall and coworkers [14–16] using X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and high resolution electron energy loss spectroscopy (HREELS). The films in these studies were prepared by dosing the Ni(100) surface with oxygen at room temperature followed by annealing at 800 K. The HREELS and LEED results of Hall and coworkers indicate that annealing to 800 K results in two surface phases, one consisting of NiO and a second consisting of a c(2 × 2)-O ordered phase. The reactivity of the NiO surface towards methane was determined using time resolved XPS at pressures of 8×10^{-5} Torr and temperatures of 700–800 K. The reaction probability of methane with the NiO film was higher than that observed for the Ni(100) surface. Also it was determined that the NiO phase was more reactive than the c(2 × 2)-O phase [14–16].

The goal of the present research was to assess the relative importance of the precursor mediated dissociative pathway versus the direct dissociative pathway for the reactive sticking of methane on Ni(100) and on a model NiO thin film grown on a Ni(100) surface.

2. Experimental

These experiments were carried out in a combined elevated pressure reactor–ultrahigh vacuum system with a base pressure of $< 5 \times 10^{-10}$ Torr. The system was equipped with Auger electron spectroscopy (AES), LEED, and temperature programmed desorption (TPD) [#1].

The sample manipulator allowed for resistively heating the Ni(100) crystal to 1450 K by spotwelding the sample to W support leads. The surface temperature was monitored by a W/5%Re–W/26%Re thermocouple spotwelded to the sample edge. The surface was cleaned using either one of two methods. In the first method the sample was annealed for 2 min at 1475 K in 5×10^{-8} Torr of oxygen and then placed in the high pressure reactor for 5 min in 1 Torr hydrogen at 1175 K. In the second method, the surface oxide was reduced in 1 Torr methane.

The methane (Matheson 99.99% purity) was purified following the procedure described in ref. [4]. The methane was first cooled in liquid nitrogen (LN_2) over an activated zeolite trap, then distilled into a glass bulb at 90 K whose walls had been freshly covered with a Ti film. The cleanliness of the methane and system were checked extensively using the procedures described previously [4,5].

3. Results and discussion

3.1. ACTIVATION OF METHANE ON CLEAN Ni(100)

In fig. 1 the C(272 eV)/Ni(848 eV) AES ratios are presented for a constant methane exposure of 30 Torr s at 500 K. The exposure pressures in these experiments, however, were varied between 0.05 and 1.0 Torr. For each pressure a C/Ni ratio of ≈ 0.14, corresponding to about 0.25 monolayers, was found following reaction with a slightly larger value observed for the higher pressures. This C/Ni ratio is identical within experimental error to that reported previ-

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[#1] The system is similar to that described previously [17] with the exception of the hemispherical analyzer and the associated techniques.

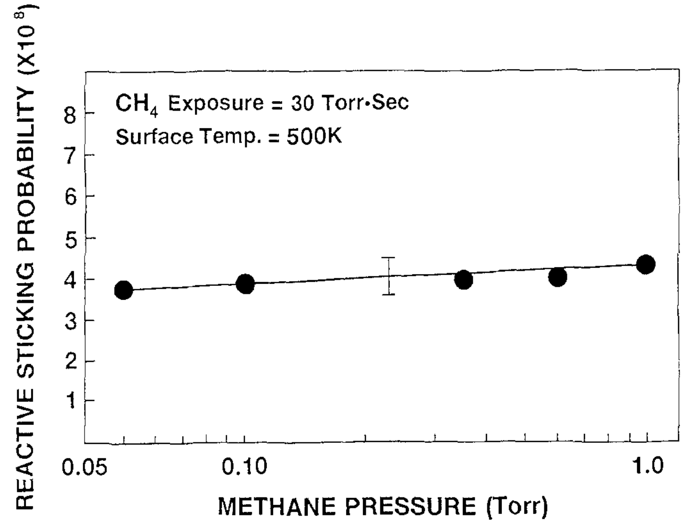

Fig. 1. Pressure dependence of the methane sticking probability for a constant methane exposure of 30 Torr s at 500 K.

ously [4]. In all experiments the lineshape of the C(272 eV) peak was carbidic in nature and was not coverage dependent.

Previous studies have shown that the activation of methane is significantly more facile on Ni(100) compared to Ni(111) and occurs on Ni(100) at pressures as low as 10^{-3} Torr [3]. This is in contrast to the Ni(111) surface which showed no activation below pressures of 0.2 Torr [5]. The results presented here for the Ni(100) surface are consistent with the activation of methane occurring through a precursor mediated activation process. That is, dissociative sticking on Ni(100), rather than occurring through a translationally "hot" methane molecule striking the surface, takes place via a mechanism in which the methane becomes thermally accommodated with the surface. Any significant role of the direct activation channel in methane reactive sticking on Ni(100) can be ruled out based upon the low pressure (< 0.2 Torr) experiments in which the methane is at room temperature.

The slight increase in the C/Ni AES ratios with pressure in fig. 1 suggests a small contribution of the direct mechanism to the methane sticking probability on Ni(100). To investigate this point further, the C/Ni ratios were determined at 450 K for constant methane exposures at 0.10 and 1.0 Torr (fig. 2). These results indicate that at 1.0 Torr the initial slope for methane activation is slightly higher than for the 0.10 Torr experiment. Since the C/Ni AES Auger ratios correspond directly to the number of surface carbon atoms [4], these data suggest that the initial sticking probability for methane on Ni(100) is slightly higher at 1.0 Torr. These results then are consistent with the direct activation mechanism contributing in a very minor way to the overall reactive sticking;

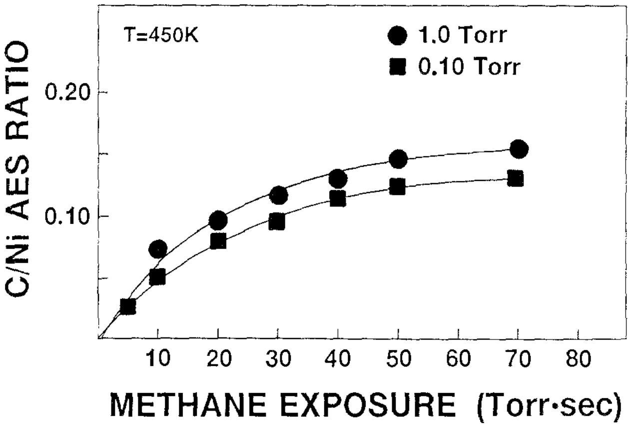

Fig. 2. C(272 eV)/Ni(848 eV) AES ratios as a function of methane exposure (Torr s) for pressures of 0.10 and 1.0 Torr at 450 K.

however, dissociative sticking of methane on Ni(100) is clearly dominated by the precursor mediated mechanism.

Recently the activation of methane on nickel has been described using a thermally assisted tunneling model [18,19]. The authors used this model to interpret experimental results for dependencies of the methane sticking probabilities on the surface and gas temperature, the incident kinetic energy and the vibrational state. Likewise the effects of isotopic substitution were addressed. A basic assumption of this model is that activation of methane occurs via a direct dissociative chemisorption mechanism. The results presented here indicate that this assumption is not warranted for the Ni(100) surface.

The sticking probability of methane on the more open Ni(110) surface is even higher than that found for the Ni(100) [4]. Indeed, the dissociative adsorption of methane has been observed for the Ni(110) surface for pressures of 10^{-2} Torr [10]. Clearly for a Ni(110) surface, a precursor mediated mechanism is likely the primary route for activation of methane.

Finally, it should be noted regarding the relevance of these studies to practical catalysis involving methane and Ni, e.g., steam reforming, that Ni(111) facets will contribute to the product only in a very minor way [4]. The majority of the product is derived from those catalyst morphologies corresponding to Ni(100), Ni(110), and other crystal faces with higher indices [4].

3.2. METHANE ACTIVATION ON OXIDIZED Ni(100)

The activation of methane on NiO was studied using thin films grown on Ni(100). The NiO films were prepared by dosing the sample with 300 L of O_2 (5×10^{-7} Torr) at ≈ 325 K and then annealing to 600 K for one minute. The passively oxidized surface resulted in a NiO(100) film that was ≈ 3.4 ML thick

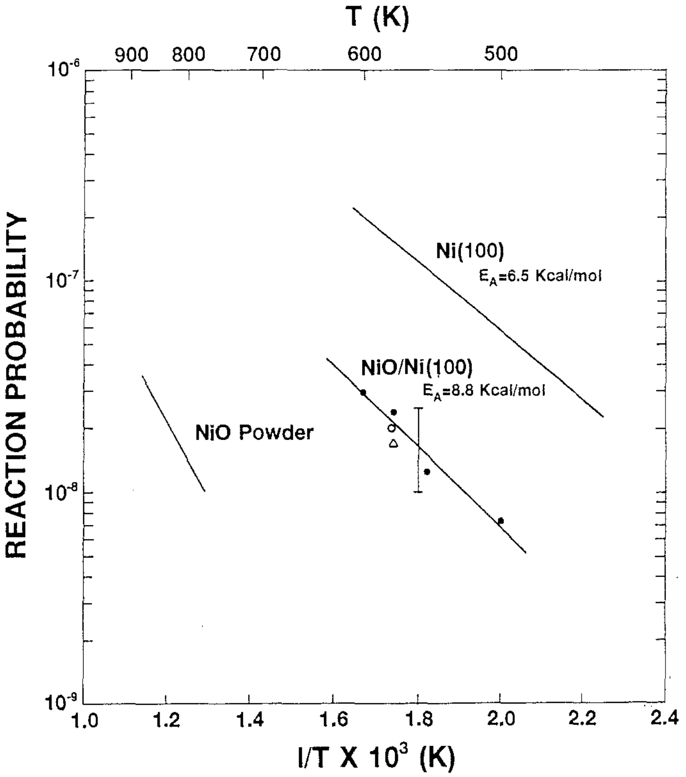

Fig. 3. Temperature dependence of the reaction probability at 1.00 Torr methane for the NiO/Ni(100) thin films. The data at 575 K is for pressures of 0.10 (○), 0.5 (△) and 1.0 Torr (●) at a constant methane exposure of 45 Torr s. Also, presented is the reaction probability for methane activation on Ni(100) [4] and methane oxidation on NiO powder (25% methane, 12.5% O_2, 67.5% Ar, 1 atm total pressure) [15].

and consisted of an areal density of 3.9×10^{15} oxygen atoms/cm^2 [20]. Annealing the sample resulted in a surface consisting of a NiO phase and a c(2 × 2)-O phase [14]. NiO surfaces prepared by this method were utilized to estimate the reaction probabilities of methane and the results obtained are presented for a constant pressure of 1 Torr and temperatures of 500–600 K in fig. 3. The reaction probabilities were calculated using the change in the AES O/Ni intensities as a function of time and assuming that the initial oxygen coverage was linear with intensity. It was also assumed that each methane molecule reacted with three surface oxygen atoms, producing one molecule of CO and two molecules of water [14]. From the reaction probabilities an apparent activation energy of 8.8 ± 1.1 kcal/mol was obtained for the dissociation of methane. This is very close to the value measured for the clean Ni(100) surface [4].

The methane reaction probabilities for the NiO film are between those values measured for the Ni(100) surface [4] and those found for a NiO powder (25%

methane, 12.5% oxygen, 67.5% argon, 1 atm total pressure) [15] as shown in fig. 3. On the basis of the similarities in the apparent activation energies for the NiO films and the Ni(100) surface, a model is proposed in which the activation of methane is occurring at metallic Ni sites on the NiO film. The order of magnitude lower reaction probabilities for the NiO/Ni(100) sample relative to the Ni(100) suggests a Ni defect density on the NiO surface of ≈ 10%. This is consistent with a recent scanning tunneling microscope study in which a defect density of 20–25% was observed for NiO [21].

Experiments were carried out to demonstrate the similarities between methane activation on Ni and NiO. Methane reactive sticking was measured for the NiO films at 575 K and pressures of 0.1, 0.5 and 1.0 Torr with a constant methane exposure of 45 Torr s (fig. 3). The reactivity of the NiO surface at 0.10 and 0.50 Torr was identical, within experimental error, to the 1.0 Torr data. This correlation is consistent with a precursor mechanism dominating the reactive sticking of methane on the NiO films and also is consistent with the Ni defect reaction site model of NiO described above.

The reaction probabilities reported here for methane on NiO are significantly lower than those recently published [15]. The origin of this discrepancy is at present unclear, however, the results of the present study indicate that trace amounts of hydrogen or CO in the methane gas can lead to a significant error in the apparent methane sticking probabilities. The very careful cleaning procedure used in the present studies, for example, was shown to be essential in order to minimize any contribution from hydrogen or CO.

4. Conclusion

(1) The activation of methane on the Ni(100) surface very likely occurs through a precursor mediated mechanism. This contrasts with a direct mechanism for methane sticking on the Ni(111) surface.

(2) The reactivity of methane on a NiO thin film is similar to that for the clean Ni(100) surface with an apparent activation energy of 8.8 ± 1.1 kcal/mol. The reaction on NiO is proposed to occur on metallic Ni defect sites.

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