High-resolution electron energy-loss measurements of sticking coefficients of methane decomposition on Ru(0001)

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Abstract

A new approach, utilizing an elevated pressure reactor and high-resolution electron energy loss spectroscopy (HREELS), to the measurement of sticking coefficients of methane decomposition on Ru(0001) has been demonstrated. It has been shown that the detection, by Auger electron spectroscopy and photoelectron spectroscopy, of fractional monolayers of carbon on ruthenium is difficult because of the interference of the substrate signals. HREELS thus offers new opportunities to measure carbon buildup kinetics on ruthenium crystals. The measured initial sticking coefficient for methane decomposition on Ru(0001) varies from 1.7-12.7 \times 10^{-7} in the 500-650 K temperature range. The apparent activation energy for methane dissociation is found to be 8.5 kcal/mol.

1. Introduction

The dissociative chemisorption of methane on various metal catalysts is an important subject of current catalytic research. Several studies using molecule beam techniques have demonstrated the importance of translational kinetic energies in methane decomposition [1-5]. Rettner et al. [1], for example, have reported a five-order-of-magnitude increase in the initial dissociative chemisorption probability of CH₄ on W(110) when the CH₄ incident translational energy is increased from 2.4-24.0 kcal/mol. For methane decomposition on Ni(111) surfaces, Beebe et al. [6] have found an agreement in both the absolute value of the initial sticking coefficients and the apparent Arrhenius activation energies between their elevated pressure study and the molecule beam measurements [6]. For gas pressures (1-100 Torr) employed in an elevated pressure study, an equilibrated gas layer, several mean free paths in thickness, exists around the heated crystal. This gas layer is thermalized due to inelastic collisions with the surface. It is believed [6] that a small portion of the gas at the high energy tail of the Maxwell-Boltzman distribution gains sufficient thermal energies to overcome the activation barrier to dissociation. Obviously the molecule beam approach permits a much greater degree of control in various parameters, such as translational kinetic energies and incidence angles of the beam. However, a shortcoming for this technique is the
difficulties encountered in generating a molecule beam with very low kinetic energies and with a sufficient flux to measure dissociative sticking at very low sticking probabilities \( < 10^{-7} \). The low energy molecular beams are required in these experiments in order to mimic catalytic processes at high pressures where a major fraction of the molecules has very low translational energies.

In this Letter, we present a new approach to the measurement of initial sticking coefficients of methane decomposition on ruthenium surfaces. This approach utilizes an elevated pressure reactor and high-resolution electron energy-loss spectroscopy (HREELS). The carbon buildup kinetics of hydrocarbon decomposition on transition metal surfaces have been traditionally studied using Auger electron spectroscopy (AES) [3–8]. However, it has been shown that the detection, by Auger electron spectroscopy [9] and photoelectron spectroscopy [10–11], of fractional monolayers of carbon on ruthenium is difficult because of the interference of the substrate signals. In the present study, HREELS has been used to identify surface hydrocarbonaceous intermediates formed from methane decomposition and to measure the carbon buildup kinetics on Ru(0001).

2. Experimental details

The studies were carried out in a combined elevated-pressure reactor/ultrahigh vacuum (UHV) system, described elsewhere [12], equipped with HREELS, AES, low energy electron diffraction (LEED) and temperature programmed desorption (TPD), and for sample heating and cooling. After completion of surface cleaning in the surface analytical chamber, the single-crystal Ru catalyst could be transferred in situ into the reaction chamber through a double-stage differentially pumped teflon sliding seal. The details of crystal cleaning and handling can be found elsewhere [12].

Methane gas, 99.996%, was purified by (1) storage in a zeolite trap cooled with liquid nitrogen; (2) release of CH4 by warming up this trap until the desired CH4 pressure was obtained in the manifold; (3) subsequent storage in a glass bulb whose inner wall was coated with freshly deposited titanium. To facilitate better control of the length of reaction time, methane gas was mixed in an Ar matrix with an Ar:CH4 ratio of 150:1. Argon gas, 99.9995%, was purified with a similar procedure.

![HREELS spectra](image)

Fig. 1. HREELS spectra acquired following methane decomposition on Ru(0001) at two representative reaction temperatures: (a) 500 K and (b) 600 K. The reaction was carried out with 5 Torr of methane for 170 s. The spectra were collected at \( E_p = 4.1 \) eV and at the specularly reflected beam direction.
To measure carbon buildup kinetics, the following procedure was used: (1) the mixture of Ar and CH$_4$ was introduced into the reactor with the clean crystal at $T < 330$ K; (2) the crystal temperature was quickly raised to a reaction temperature where it was held for the length of that particular reaction; (3) heating was turned off simultaneously while exhausting the gases and (4) the crystal was transferred to the HREELS position of the surface analytical chamber.

HREELS data then were collected following the above procedure. The spectra were acquired using an electron beam with a primary energy of $E_p = 4.1$ eV and at an incident angle of the electron beam of 60° about the surface normal.

3. Results and discussion

Displayed in Fig. 1 are HREELS spectra acquired following methane decomposition on Ru(0001) at two representative reaction temperatures. The reaction of CH$_4$ with Ru(0001) was carried out in the reaction chamber with 5 Torr of pure methane for 120 s. For the gas pressure employed here, the gas temperature, $T_{CH_4}$, in vicinity of the heated Ru crystal is equal to the sample temperature [6]. Exposing the surface to methane gives rise to several distinct loss features in the 200–4000 cm$^{-1}$ frequency range of the HREELS spectra. At $T_{CH_4} = 600$ K, the observed loss features exhibit a distinct loss intensity pattern, i.e. an intense loss peak at 790 cm$^{-1}$ and a weak feature at 3000 cm$^{-1}$. This set of loss features is a signature for a methylidyne species (CH); the loss features at 790 and 3000 cm$^{-1}$ are attributed to the CH bending, $\delta$(CH), and the CH stretching, $\nu$(CH), mode, respectively, of the CH$_2$ species [12–20]. In addition to the loss features associated with the CH species, two weaker loss peaks at 1160 and 1395 cm$^{-1}$ are evident at $T_{CH_4} = 500$ K, as shown in spectrum (a) of Fig. 1. In a separate article [12], the losses at 1160 and 1395 cm$^{-1}$ have been attributed to the carbon–carbon stretch ($\nu$(C=C)) and the CH$_2$ scissors ($\delta$(CH$_2$)), respectively, of a vinylidene intermediate (CCH$_2$). The possibility for the assignment of the two losses to a surface species containing CH$_3$ groups is rejected since the symmetric (at $\sim 1350$ cm$^{-1}$) and asymmetric (at $\sim 1425$ cm$^{-1}$) deformation modes of CH$_3$ were not observed. Furthermore, the corresponding spectrum acquired at an off-specular direction (not shown here) revealed only one peak at $\sim 1400$ cm$^{-1}$ that is attributed to the scissor-mode of a CH$_2$ group. The assignment of these two losses to a methylidene (CH$_2$) species is also rejected because a CH$_2$ species is not stable on Ru surface in the 500–500 K temperature range [12]. It has also been found [12] that the methylidyne species is present on the Ru(0001) surface over a wide temperature range (between approximately 400–700 K), whereas the vinylidene species is less thermally stable than the methylidyne species and is present only at temperatures between 500–550 K. At $T_{CH_4} < 400$ K (not shown here), methane decomposition becomes negligible [12]. At temperatures exceeding 800 K, the reaction of methane on the Ru(0001) surface produces exclusively graphitic carbon [12].

Two weak loss features arising from adsorbed CO, are noticeable in spectrum (a) of Fig. 1. Considering the high cross section of CO vibrational modes, the coverage of the CO impurities is estimated to be negligibly low.

Since the vinylidene intermediates are seen only below $T_{CH_4} = 550$ K and, furthermore, the loss intensities of this species is an order of magnitude lower than that of the $\delta$(CH) mode of the methylidyne intermediates, methane decomposition kinetics can be followed by measuring the intensity of the $\delta$(CH) mode of the methylidyne species.

Fig. 2 shows the $\delta$(CH) intensity plotted versus the reaction time at various reaction temperatures, $T_{CH_4}$. The reactions were carried out with 5 Torr of the mixture of CH$_4$ and Ar at an Ar:CH$_4$ ratio of 150:1. The $\delta$(CH) mode intensities plotted here are those divided by their respective background levels rather than those normalized to the elastically reflected beam. The background level of a loss feature was determined by directly measuring the count between the smooth base line of the spectrum and the zero line. The reason for this is that the acceptance angle of the HREELS spectrometer is usually smaller than
the angular distribution of the elastically scattered beam. When surface ordering varies, the elastic peak changes in shape and intensity, and therefore the ratio of the loss peak to the elastic peak has no real measure of the intensity. It has been shown [21], however, that the loss intensity divided by its background is independent of the state of ordering on the surface and thus is proportional to quantities of adsorbed molecules at submonolayer coverages.

The initial sticking coefficient for methane decomposition on Ru(0001) may be obtained from the initial slope of each plot in Fig. 2. This quantity is defined in our case as the ratio of the number of CH$_4$ molecules which collide with the surface and dissociate (to form primarily methylidyne species), to the number of the molecules which collide with the surface. The numerator of this ratio can be obtained from the rate of carbon buildup, which is approximated by the rate of increase in methylidyne surface coverage. In the present case, the saturation or monolayer coverage of the CH species is assumed to correspond to the surface density of Ru(0001) (1.577 × 10$^{15}$ cm$^{-2}$). This assumption sets an upper limit for the CH surface coverage and thus may overestimate the sticking coefficient. Consistent with this assumption, however, our CO adsorption experiments revealed that the integrated area of CO thermal desorption spectra from the methylidyne saturated surface is only 9% of that from the clean surface. The denominator of the sticking coefficient can be determined by knowing the incident flux of methane molecules. At a given pressure, $P$, and temperature, $T$, the rate of molecules impinging on a surface, $N$, can be computed with the formula: $N$(molecules cm$^{-2}$ s$^{-1}$) = 3.52 × 10$^{22}$ $P$ (Torr)/[$M$ (g mol$^{-1}$) $T$ (K)]$^{1/2}$. This method requires knowledge of the temperature of the gas in vicinity of the heated crystal. For the sticking coefficient data presented below, we assume that the gas temperature, within a distance from the Ru(0001) surface that is a few times the mean free path of methane, is equal to the surface temperature. This condition is satisfied for gas pressures employed in the present study [6].

Fig. 3 shows the initial sticking coefficients of methane decomposition on Ru(0001) plotted as a function of the inverse reaction temperature, 1/T$_{CH_4}$, obtained using the above procedure. Also included are those measured from low index planes of Ni crystals using AES [6]. The apparent activation energy for methane decomposition on Ru(0001) may be deduced from the slope of the plot in Fig. 3. The obtained value of 8.5 kcal/mol compares favorably with that (6.2 kcal/mol) derived from silica supported Ru catalysts [22]. The apparent activation energies for methane decomposition on various transition metals have been found to vary from 6.0–14.4 kcal/mol [1,3,4,6,22].
In summary, the present study has demonstrated the capabilities of HREELS in measuring carbon buildup kinetics on Ru(0001) surfaces. This new method allows kinetics of dissociative chemisorption of hydrocarbons on some transition metal surfaces, such as Ru and Pd surfaces, to be studied without the interference from the substrate signals which is encountered in AES and photoelectron spectroscopy measurements.

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5. References