The detection, by Auger electron spectroscopy (AES), of fractional monolayers of carbon on Ru is difficult because of the interference between the Ru (273 eV) and C (272 eV) transitions [1,2]. In attempting to deal with this problem, two methods of analysis have been used. In the first, the ratio of the 273 eV signal (p–p height) to the 231 eV Ru signal is monitored [3,4]. Because the 231 eV signal is from Ru, unencumbered by C, this ratio grows as carbon accumulates. In the second method, the ratio $R^*$ of the positive to the negative portions of the signal at 273 eV is taken [5]. Since the C signal is dominated by a negative feature, while the Ru signal is more nearly symmetrical, this ratio decreases as the surface carbon concentration increases. Neither of these methods is very precise and neither can be reliably used to monitor low levels of carbon. As part of a continuing series of studies of the catalytic methanation reaction $(3H_2 + CO \rightarrow CH_4 + H_2O)$ [6], we report here the observation and measurement of an AES feature that arises from that form of carbon, customarily called carbodic carbon [6], which is active in the methanation reaction over single crystal Ru(110) [7]. This feature can be followed easily at low carbon levels and used for semi-quantitative study of the kinetics of the carbide build-up and removal steps in the methanation reaction.

The experiments reported here used a high-pressure reaction chamber linked to an UHV analysis chamber that has been described previously [6]. The Ru(110) sample was cleaned using high temperature oxidation at $10^{-6}$ Torr O$_2$ followed by heating in vacuum to 1570 K [8].

In fig. 1, AES spectra in the Ru–C region are shown for (a) a clean surface and (b) a surface exposed to 10 Torr of CO at 550 K for 1000 s. Small amounts of carbon have little influence on the signals at 231 and 273 eV, but in the region between 245 and 265 eV two small peaks appear on the rising portion of the 273 eV signal. The energies of these features (251 and 259 eV) are identical to carbodic carbon features found on Ni [6]. The 259 eV signal may contain contributions
Fig. 1. Auger electron spectra in the ruthenium and carbon regions: (a) clean Ru and (b) Ru exposed to 10 Torr CO at 550 K for 1000 s. The region between 240 and 260 eV is expanded by a factor of 50. The transitions at 251 and 259 eV are assigned to carbide. When the carbide is removed, the strong transition at 231 eV is unaffected whereas that at 273 eV shows a relative decrease of its negative portion.

from both Ru and C, but the 251 eV feature is easily resolved from Ru and has useable signal-to-noise character. Moreover, it is well-behaved kinetically and can be used to follow carbide build-up and removal rates. A detailed report of these kinetics will be reported elsewhere [7], but as an example, fig. 2 shows the temperature dependence of the carbide formation rate. The experiments all involve treatment in the reaction chamber at 10 Torr CO for the reaction time and temperature shown. After evacuation and insertion into the UHV chamber, the sample was flashed briefly to 600 K to remove residual CO, and the peak height ratio of the C (251 eV) to the Ru (231 eV) signal was taken as a measure of the active carbon level and plotted on the ordinate of fig. 2. Three features are noteworthy: (1) the carbide build-up can be followed easily for $T < 550$ K; (2) the rate of carbide build-up is strongly temperature dependent; and (3) an inactive carbon forms readily at high $T$ as evidenced by a decreasing value of $R^*$ accompanied by the loss of the 251 eV carbide signal. We take this inactive carbon to be graphitic as shown for Ni [6].

The hydrogenation of the carbidic carbon can be followed readily [7]. Further-
more, the specific rate of carbide formation, calculated from the data of fig. 2, is equal to the rate of methane formation in a CO—H2 mixture [7]. Similar results have been reported for Ni where, under similar conditions, one-half monolayer of carbide is formed [6].

In summary, we have found an AES feature, assigned to carbidic carbon, which is separable from Ru features and can be used to follow active carbon levels associated with various steps in the methanation reaction.

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References