

## SHOP NOTES

These are "how to do it" papers. They should be written and illustrated so that the reader may easily follow whatever instruction or advice is being given.

### An accurate and simple method of measuring relative mass spectrometric sensitivities

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We describe an accurate and convenient method of determining the relative mass spectrometric sensitivities of various species by using surface decomposition reactions to generate these species in known stoichiometric ratios *in situ* in vacuum systems. In particular, we have used the decomposition reactions of formaldehyde and formic acid on Ru(001) to determine the relative mass spectrometric sensitivities of H<sub>2</sub>, HD, D<sub>2</sub>, and CO.

It is often necessary to determine the relative or absolute mass spectrometric sensitivities of various molecules in rate measurements of heterogeneously catalyzed reactions, as well as in other applications. For example, in studying the kinetics and mechanism of formic acid decomposition on the Ru(001) surface in order to determine the selectivity of this surface for dehydration (decomposition to CO and H<sub>2</sub>O) and dehydrogenation (decomposition to CO<sub>2</sub> and H<sub>2</sub>), knowledge of the relative mass spectrometric sensitivities of CO and H<sub>2</sub> was required.<sup>1</sup> The absolute mass spectrometric sensitivities of H<sub>2</sub>, HD, and D<sub>2</sub> must be known in order to calculate the absolute rate of HD production and the reaction probability in measurements of the kinetics of isotopic exchange of H<sub>2</sub> and D<sub>2</sub>,<sup>2</sup> and in order to perform mass balance studies of the coadsorption of D<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>.<sup>3,4</sup>

In the high pumping speed limit, the absolute rate of production of species x ( $R_x$ ) and its mass spectrometric intensity ( $I_x$ ) are related by

$$R_x = \frac{S_x}{k_B T_g} \eta_x I_x, \quad (1)$$

where  $S_x$  is the pumping speed of species x,  $T_g$  is the gas temperature, and  $k_B$  is the Boltzmann constant. The quantity  $\eta_x$  is a proportionality constant defined in such a way that the partial pressure  $P_x$  is given by  $P_x = \eta_x I_x$ . It is often termed the mass spectrometric sensitivity. Since we are concerned with the relation between the absolute rate and the mass spectrometric intensity in kinetic studies of heterogeneously catalyzed reactions, we define the absolute mass spectrometric sensitivity  $\beta_x$  as

$$\beta_x \equiv \frac{k_B T_g}{S_x \eta_x}. \quad (2)$$

In the following discussion, we also define the relative mass spectrometric sensitivity of species x as

$$\gamma_x \equiv \beta_x / \beta_{H_2}; \quad (3)$$

thus  $\gamma_{H_2}$  is unity. The choice of hydrogen as a reference here is completely arbitrary. From Eqs. (1)–(3), we find that

$$\gamma_x = \frac{S_{H_2}}{S_x} \frac{\eta_{H_2}}{\eta_x}, \quad (4)$$

$$\gamma_x = \frac{R_{H_2}}{R_x} \frac{I_x}{I_{H_2}}, \quad (5)$$

and

$$R_x = \frac{I_x}{\gamma_x \beta_{H_2}}. \quad (6)$$

To compare the relative production rates of species x and y, one has to divide the mass spectrometric intensities of x and y ( $I_x$  and  $I_y$ ) by their relative mass spectrometric sensitivities, i.e.,  $R_x : R_y = I_x / \gamma_x : I_y / \gamma_y$  [cf., Eq. (6)].

The relative mass spectrometric sensitivity of species x ( $\gamma_x$ ) is proportional to the ratio of pumping speeds of hydrogen and species x ( $S_{H_2}/S_x$ ) and the ratio of the proportionality constants of hydrogen and species x ( $\eta_{H_2}/\eta_x$ ) [cf., Eq. (4)]. The proportionality constant  $\eta_x$  is a function of the ionization probability of species x in the ionizer of the mass spectrometer,<sup>5</sup> the transmission probability of the ions through the mass spectrometer (which remains relatively constant up to amu 20 and then falls off by approximately one decade per 150 amu for our UTI 100C quadrupole mass spectrometer), and the electron multiplier gain of the ions generally considered to have an  $M^{-1/2}$  dependence, where  $M$  is the ion mass. The ratio  $\eta_{H_2}/\eta_x$  is obviously independent of the system configuration since it is an intrinsic property of the mass spectrometer. The ratio of pumping speeds  $S_{H_2}/S_x$ , however, depends upon the system configuration. For example, for an ion pumped vacuum system with a poppet valve separating the vacuum chamber and the ion pump, the ratio of the pumping speeds  $S_{H_2}/S_x$  would be different for a system configuration with the poppet valve wide open and for a

system configuration with the poppet valve partially closed. Each time one changes the system configuration in any way, the relative mass spectrometric sensitivities must be remeasured. Thus, an accurate yet simple method of determining the relative mass spectrometric sensitivity would be very helpful. We present here a method of determining the relative mass spectrometric sensitivities, particularly those of H<sub>2</sub>, HD, D<sub>2</sub>, and CO by introducing into the vacuum CO + H<sub>2</sub>, or CO + D<sub>2</sub>, or H<sub>2</sub> + HD + D<sub>2</sub> + CO stoichiometrically (i.e., with known rate ratios) via chemical decomposition reactions on the Ru(001) surface.

The system we have employed in the measurement of rates of catalytic reactions is an ion pumped ultrahigh vacuum (UHV) system, equipped with quadrupole mass spectrometry and a directional beam doser.<sup>1,6</sup> In the steady-state rate measurements, the reactant is introduced into the UHV system through the directional beam doser. The Ru(001) surface is positioned in and out of the reactant beam at a constant surface temperature, and the increase in the intensities of the products and the decrease in intensity of the reactant are monitored mass spectrometrically.

Formaldehyde (H<sub>2</sub>CO) decomposes on the Ru(001) surface only to H<sub>2</sub> and CO.<sup>6</sup> Hence the steady-state decomposition of H<sub>2</sub>CO is equivalent to leaking an equimolar mixture of CO and H<sub>2</sub> into the UHV system. The relative mass spectrometric sensitivity of CO ( $\gamma_{\text{CO}}$ ) can be determined simply by taking the ratio of the mass spectrometric intensities of CO ( $I_{\text{CO}}$ ) to H<sub>2</sub> ( $I_{\text{H}_2}$ ), measured during the steady-state decomposition of H<sub>2</sub>CO since  $R_{\text{H}_2} = R_{\text{CO}}$ , i.e.,  $\gamma_{\text{CO}} = I_{\text{CO}}/I_{\text{H}_2}$  [cf., Eq. (5)]. The increase in the intensity of mass 28 ( $\Delta I_{28}$ ) is the sum of an increase of CO intensity and a decrease in the partial pressure of H<sub>2</sub>CO, due to the H<sub>2</sub>CO decomposition (measured by the decrease in the mass 29 intensity,  $\Delta I_{29}$ ; the peak at  $m/e = 29$  is the most intense one in the mass spectrum of H<sub>2</sub>CO). The cracking pattern of H<sub>2</sub>CO can be measured easily, and in our UHV system the H<sub>2</sub>CO exhibits  $m/e$  peaks at 30, 29, and 28 with intensity ratios of 0.73:1.00:0.34, in good agreement with previously reported values.<sup>7</sup> Thus, the mass spectrometric intensity of CO is given by  $I_{\text{CO}} = \Delta I_{28} + 0.34|\Delta I_{29}|$ . The determination of the true mass spectrometric intensity of H<sub>2</sub> is straightforward. It is simply the increase in the intensity of mass 2 ( $\Delta I_2$ ) when the Ru(001) surface is positioned in the H<sub>2</sub>CO beam, since the H<sub>2</sub>CO molecule has negligible mass 2 cracking fragment. The result is  $\gamma_{\text{CO}} = I_{\text{CO}}/I_{\text{H}_2} = 0.98$ . Similarly, the relative mass spectrometric sensitivity of D<sub>2</sub> was determined by using D<sub>2</sub>CO. We find in this case

$$\gamma_{\text{D}_2}:\gamma_{\text{CO}} = I_{\text{D}_2}:I_{\text{CO}} = 0.65:0.98.$$

It is known that during the steady-state decomposition of DCOOH on Ru(001) at high surface temperatures, the production rates of H<sub>2</sub>, HD, and D<sub>2</sub> have a ratio of 1:2:1.<sup>1</sup> The steady-state decomposition of DCOOH on Ru(001) at high surface temperatures is equivalent to leaking H<sub>2</sub>, HD, and D<sub>2</sub> with a stoichiometry of 1:2:1 into the UHV system.<sup>8</sup> The relative mass spectrometric sensitivities of H<sub>2</sub>, HD, and D<sub>2</sub> may be determined easily by taking the ratio of the properly weighted mass spectrometric intensities of H<sub>2</sub> ( $I_{\text{H}_2}$ ), HD ( $I_{\text{HD}}$ ), and D<sub>2</sub> ( $I_{\text{D}_2}$ ) according to Eq. (5), i.e.

$\gamma_{\text{H}_2}:\gamma_{\text{HD}}:\gamma_{\text{D}_2} = I_{\text{H}_2}:0.5I_{\text{HD}}:I_{\text{D}_2}$ . The relative mass spectrometric sensitivities thus determined are  $\gamma_{\text{H}_2}:\gamma_{\text{HD}}:\gamma_{\text{D}_2} = 1.00:0.80:0.60$ . Note that the relative mass spectrometric sensitivity of D<sub>2</sub> is in good agreement with the value determined from the formaldehyde experiments described above. We conclude that the relative mass spectrometric sensitivities of H<sub>2</sub>, HD, D<sub>2</sub>, and CO is

$$\gamma_{\text{H}_2}:\gamma_{\text{HD}}:\gamma_{\text{D}_2}:\gamma_{\text{CO}} = 1.00:0.80:0.63:0.98$$

for our system configuration. Note that the relative mass spectrometric sensitivity of D<sub>2</sub> is an average of the two results obtained from D<sub>2</sub>CO and DCOOH.

The relative mass spectrometric sensitivities of H<sub>2</sub>, HD, D<sub>2</sub>, and CO can also be determined by decomposing an equimolar mixture of H<sub>2</sub>CO and D<sub>2</sub>CO on Ru(001), assuming statistical mixing of H and D on the surface. When steady state is achieved,

$$\gamma_{\text{H}_2}:\gamma_{\text{HD}}:\gamma_{\text{D}_2}:\gamma_{\text{CO}} = I_{\text{H}_2}:0.5I_{\text{HD}}:I_{\text{D}_2}:0.25I_{\text{CO}},$$

and the experimentally measured mass spectrometric sensitivities in this case are

$$\gamma_{\text{H}_2}:\gamma_{\text{HD}}:\gamma_{\text{D}_2}:\gamma_{\text{CO}} = 1.00:0.83:0.60:0.95,$$

in good agreement with the values determined above. To obtain the absolute mass spectrometric sensitivities of these species, one needs merely evaluate it for any one of them.

In summary, we have presented a convenient method of determining the relative mass spectrometric sensitivities of various species (and those of H<sub>2</sub>, HD, D<sub>2</sub>, and CO in particular), by introducing them into an UHV system stoichiometrically via surface chemical reactions. One may, of course, use calibrated sources to determine the relative and absolute mass spectrometric sensitivities. The method we have described is much easier, however. This method is obviously not limited to the decomposition of formaldehyde and formic acid on a Ru(001) surface. The concept of using surface decomposition reactions to generate various species in known stoichiometric ratios *in situ* in an UHV system to calibrate mass spectrometers is very useful.

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<sup>8</sup>High surface temperature here implies above 500 K, where the rate of decomposition of formic acid is first order in pressure. Usually, a surface temperature above that at which hydrogen desorbs will be sufficiently high to ignore kinetic isotope effects (hydrogen vs deuterium), but this issue must be considered for each system employed.