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Journal of Catalysis 221 (2004) 313–318

JOURNAL OF CATALYSIS

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The determination of desorption rate constants by monitoring of the time dependence of the decay of infrared bands—dynamic infrared spectroscopy

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Received 22 April 2003; revised 29 July 2003; accepted 29 July 2003

Abstract

A method which we have termed “dynamic infrared spectroscopy” that allows the determination of the value of the desorption rate constant of a specified adsorbate by monitoring the decay with time of the intensity of a given infrared band at a fixed temperature is described. By assuming a value of $10^{13}\ \mathrm{s}^{-1}$ it is possible to determine the value of the desorption activation energy from the value of the rate constant. The method is demonstrated for the evaluation of the desorption rate constant and the activation energy of desorption of a bidentate formate species adsorbed on polycrystalline copper. The measurement of the rate constant at different temperatures allows evaluation of the desorption activation energy without assuming a value of $10^{13}\ \mathrm{s}^{-1}$ for the desorption pre-exponential term. The method is valid only for a first-order desorption process. The method can be extended to second-order desorption processes by calibrating the intensity of the given infrared band against the coverage.

Keywords: Dynamic infrared spectroscopy

1. Introduction

Infrared spectroscopy occupies a unique position in surface science and catalysis for the identification of the configuration of adsorbates on surfaces by the measurement of their vibration spectra. While it is possible to relate a given absorbance to a predetermined coverage, the method is generally used qualitatively as one of indentification.

Determination of the kinetics of fundamental surface processes is usually achieved using other techniques. In the important area of desorption kinetics, the method of choice is temperature-programmed desorption (TPD). While this technique is ideally suited to this kinetic measurement, identification of the structure of complex adsorbates is done somewhat inferentially, usually with reference to the stoichiometry of the coincidentally desorbing species detected in the mass spectrometer [1]. The nature of the bonding of that adsorbate to the surface requires cross correlation with infrared spectroscopy.

For example, after a CO_2/H_2 mixture (1:1, 101 kPa, 25 $\mathrm{cm}^3\ \mathrm{min}^{-1}$) was dosed onto Cu supported on SiO_2 for 30 min at 388 K, by temperature programming two desorption peaks were observed of CO_2 and H_2, desorbing coincidentally at 410 and 440 at a ratio of 1:2. The stoichiometry of the desorbing species was HCO_2 and so the adsorbed species was designated to be a formate [1]. That was the limit of the information provided by temperature-programmed desorption; the technique could not make any comment on the origin of the two peak maxima of 410 and 440 for the same CO_2/H_2 co-desorbing species.

It required the application of temperature-dependent infrared spectroscopy to identify the nature of the bonding of the two species to the Cu; the 410 K peak was assigned to a monodentate formate species and the 440 K peak was assigned to a bidentate formate [1].

The ideal situation would be if infrared spectroscopy could be used in some dynamic time/temperature-dependent mode both for the identification of the bonding of a given adsorbate and for the simultaneous determination of the desorption kinetics of that specifically identified adsorbate. This paper describes a technique in which the time dependence of the loss of intensity of a given infrared band at

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doi:10.1016/j.jcat.2003.07.015

a specified temperature is used to calculate the desorption rate constant and the desorption activation energy of an unambiguously identified adsorbate. It is described in this paper for the determination of the desorption kinetics of a bidentate formate species adsorbed on unsupported polycrystalline Cu.

2. Experimental

2.1. Apparatus

Two types of apparatus were used: (i) a multipurpose microreactor system and (ii) an infrared spectrometer.

2.2. The multipurpose microreactor

The multipurpose microreactor has been described in detail previously [2]. It is a tubular reactor made in stainless steel and is 20 cm long and 0.4 cm in diameter. It is housed in a stainless steel heating block which is designed to allow it to be cooled to 77 K by passing liquid N_2 through it and to be temperature-programmed with a linear heating rate from 77 to 1100 K using a Newtronics controller, which controls both the flow of the liquid N_2 and the current to the heating element. The reactor is connected to a mass spectrometer (Hiden Analytical, Warrington, England) via a capillary and can follow 16 masses continuously with temperature/time.

2.3. The infrared spectrometer

The infrared spectrometer is a Magna 550 (ThermoNicolet). It is used in the diffuse reflectance mode by using a high-pressure environmental chamber and a “praying mantis” attachment (Harrick, England). It can be used in any gas mixture up to 30 atm and 673 K (Fig. 1).

2.4. The catalyst/adsorbent

The catalyst/adsorbent used was polycrystalline copper. It was prepared in situ by the reduction of polycrystalline CuO (BDH, England), which was 99.9% pure.

The reduction was effected using a H_2/He stream (5% H_2, 101 kPa, 25 $cm^3\,min^{-1}$) by raising the temperature from ambient to 510 K at 5 $K\,min^{-1}$ under that stream. The catalyst was then held at 510 K for 16 h under the H_2/He stream. The temperature was then lowered to ambient and the flow switched to He.

After reduction of the CuO, the polycrystalline Cu so produced was found to have a surface area of 2.1 $m^2\,g^{-1}$ by in situ N_2O reactive frontal chromatography [3].

2.5. The gases

The helium was supplied by Linde and was 99.999% pure. Before use it was passed through a Chromapack Gas Clean moisture filter.

The formic acid was supplied by Fisons Ltd. It was 99.5% pure. It was further purified by freeze, pump, thaw cycles. It was contained in a saturator held at 303 K. It was dosed onto the polycrystalline Cu ($\sim$0.2 g), which was also held at 303 K by bubbling He (101 kPa, 25 $cm^3\,min^{-1}$) through it. This produced a 6% mixture of formic acid in He.

3. Results and discussion

3.1. Temperature-programmed desorption

Fig. 2 is the temperature-programmed desorption spectrum obtained by dosing a HCO_2H/He stream (6% HCO_2H,

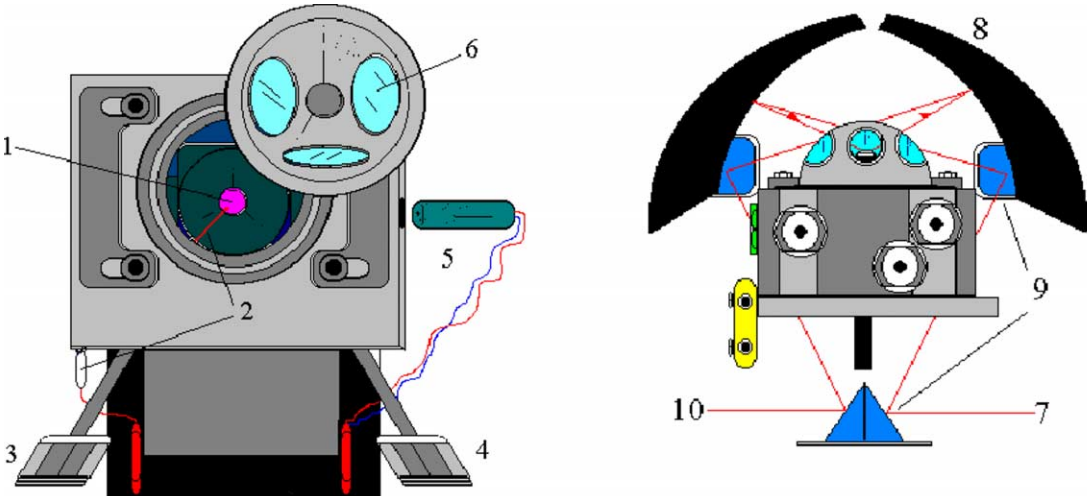

Fig. 1. Diagram of the in situ infrared cell (left) and of the “praying mantis” ellipsoidal mirror assembly (right). **1** – Catalyst, **2** – thermocouple, **3** – gas inlet, **4** – gas exit, **5** – heating cartridge, **6** – KBR window, **7** – IR beam inlet, **8** – ellipsoidal mirrors, **9** – set of mirrors to direct IR beam, **10** – IR beam to detector.

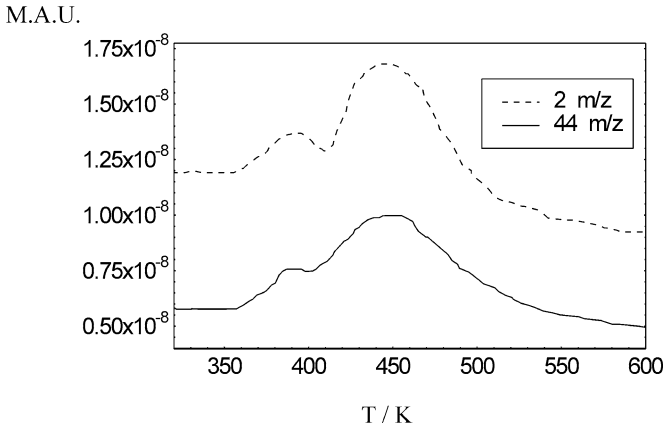

Fig. 2. The temperature-programmed desorption spectrum obtained by dosing HCO_2H/He (6% HCO_2H, 101 kPa, 25 cm^3 min^{-1}) onto polycrystalline Cu held at 303 K.

101 kPa, 25 cm^3 min^{-1}) over the polycrystalline Cu at 303 K for approximately 40 min, after which the flow was switched to He. Temperature programming at a rate of 5 K min^{-1} was begun after the He was flowed for 30 min.

Two peaks of CO_2 and H_2 are observed. The major one is at 440 K, with a minor one at 400 K. The high-temperature peak is exactly the same as that observed by co-dosing CO_2 and H_2 onto a Cu/SiO_2 catalyst. The lower one is 10 K lower than that obtained by co-dosing CO_2/H_2 onto the Cu/SiO_2 [1]. We had attributed the 410-K peak to a monodentate formate and the 440-K peak to a bidentate formate adsorbed on the Cu [1].

The peaks are deconvoluted by dropping verticals at the minimum. The mass spectrometer was calibrated against calibrated gas mixtures so that a given height of deflection of the mass spectrometer could be expressed in terms of the gas density (molecule cm^{-3}) of the desorbing species. Using this calibration and integrating the deconvoluted peaks allows the amounts of CO_2 and H_2 desorbing at 440 K in Fig. 2 to be determined as 7.9×10^{18} and 3.8×10^{18} molecule g^{-1}, respectively, corresponding to a CO_2:H_2 ratio of 2:1 or a stoichiometry of HCO_2. The species is therefore a formate. The amounts of CO_2 and H_2 desorbing at 400 K are 2.6×10^{18} and 0.9×10^{18} molecule g^{-1}, respectively—also a stoichiometry of HCO_2. On the basis of a Cu surface area of 2.1 m^2 g^{-1} the coverage of these formate species is 3.8×10^{14} (440-K peak) and 1.3×10^{14} (400-K peak) formate species/cm^2 Cu. The results obtained here confirm our earlier assignment of the 440-K and 410-K coincidentally desorbing CO_2/H_2 peaks obtained after co-dosing CO_2/H_2 onto Cu/SiO_2 as formate adsorbed onto the Cu component [1].

3.2. *Infrared spectroscopy*

Fig. 3 is the infrared spectrum of a formate species adsorbed on polycrystalline Cu. It is obtained by dosing a HCO_2H/He stream (6% HCO_2H, 101 kPa, 25 cm^3 min^{-1}) onto polycrystalline Cu held at 333 K. (The polycrystalline Cu was obtained by in situ reduction of CuO in the infrared environmental chamber using a H_2/He stream (5% H_2/He, 101 kPa, 25 cm^3 min^{-1}).) The formic acid was dosed until the bands at 1600 and 1380 cm^{-1} due to the asymmetric and symmetric C–O stretches of an adsorbed bidentate formate [4–7] became invariant with dosage of ~40 min.

The spectrum shown in Fig. 3 was taken after the dosing gas had been removed by purging the system with He (101 kPa, 25 cm^{-3} min^{-1}) for 30 min. The desorption activation energy of a bidentate formate species having a peak maximum temperature of 440 K is 122 kJ mol^{-1},

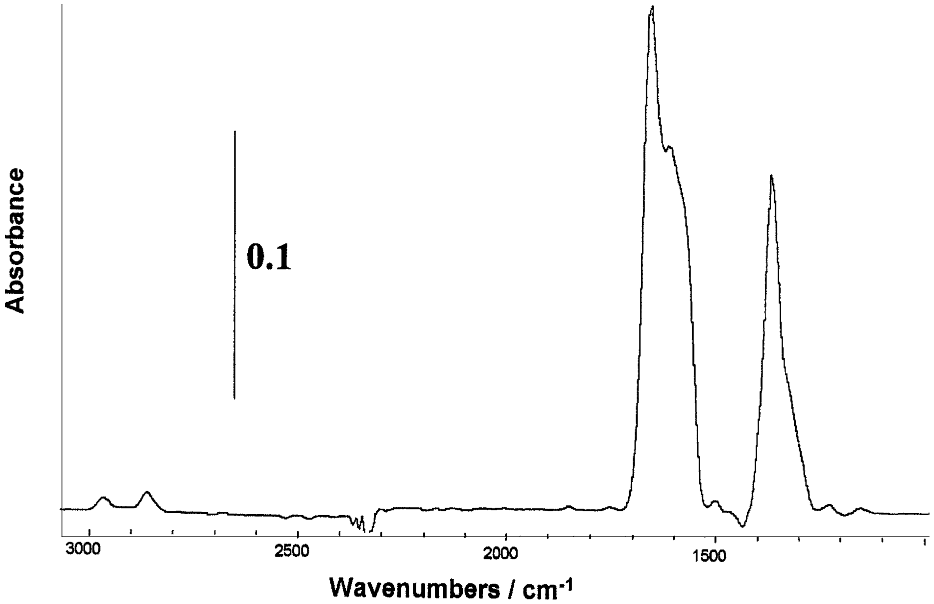

Fig. 3. The infrared spectrum of a formate species adsorbed on polycrystalline Cu.

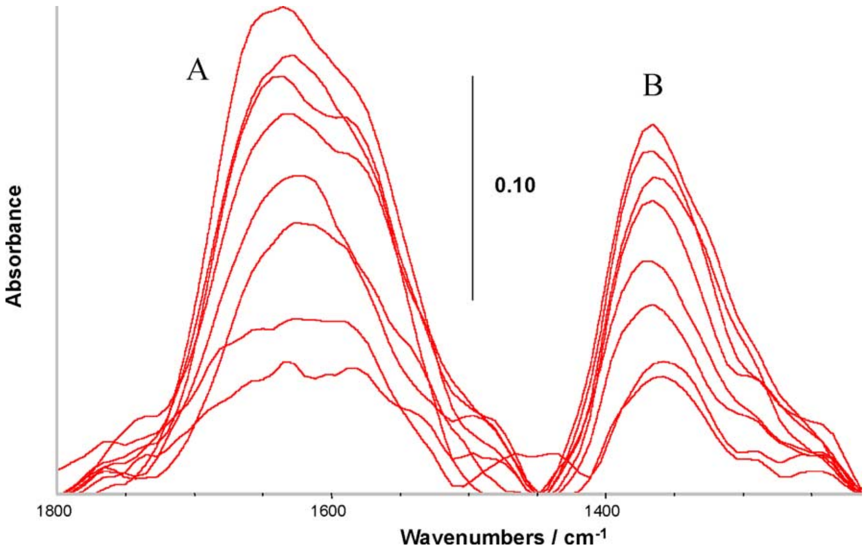

Fig. 4. The time dependence of the loss of intensity of the asymmetric OCO stretch (1600 cm^{-1}) and of the symmetric stretch (1380 cm^{-1}) of the adsorbed formate species adsorbed on polycrystalline Cu at 423 K.

a value which is obtained using the Redhead equation [8,9] and an assumed value of 10^{13} s^{-1} for the desorption pre-exponential term. On this basis the desorption half life at 333 K is $\sim 10^7$ s and so the 30-min purge in He will have no effect on the surface coverage.

As stated above the bands at 1600 and 1380 cm^{-1} are due to the asymmetric and symmetric C–O stretches respectively of a adsorbed bidentate formate [4–7]. The bands at 2850 and 2950 cm^{-1} are the C–H stretches of the bidentate formate [4,5].

The spectra shown in Fig. 4 are the asymmetric OCO stretch (1600 cm^{-1}) and the symmetric OCO stretch (1380 cm^{-1}) of a bidentate formate species adsorbed on polycrystalline copper at 423 K. The spectra are taken at arbitrary time intervals. The formic acid was dosed on, as before, from a HCO_2H/He stream (6% HCO_2H, 101 kPa, 25 cm^{-1}) until the 1600 and 1380 cm^{-1} stretches became invariant with dosing ($\sim$30 min). Having dosed the formic acid onto the polycrystalline copper, held at 423 K, to saturation, the flow was switched from the HCO_2H/He stream to He to remove the gas phase He ($\sim$10 min). (Ten minutes was the minimum period of time for the complete removal of gas phase formic acid as detected by the infrared spectrometer.)

The gas phase formic acid having been removed to avoid replenishment of the adsorbed formate by adsorption, the rate of desorption of the adsorbed bidentate formate species was measured by recording its asymmetric OCO stretch (1600 cm^{-1}) at recorded time intervals. Table 1 lists the intensities of the absorbance of these bands and the times at which they were taken.

The coverage of a given adsorbed species is proportional to the intensity of the absorbance, Abs, of that band; i.e.,

$$\mathrm{Abs} \propto \theta \tag{1}$$

Table 1

t (s)	Absorbance A	Absorbance B	ln(Abs$A$)	ln(Abs$B$)
0	0.2	0.15	−1.61	−1.89
240	0.17	0.14	−1.77	−1.96
360	0.15	0.125	−1.89	−2.08
420	0.14	0.12	−1.96	−2.12
480	0.131	0.1	−2.03	−2.31
540	0.11	0.082	−2.21	−2.5
780	0.072	0.055	−2.63	−2.9
900	0.06	0.04	−2.81	−3.21

or

$$\mathrm{Abs} = \kappa\theta, \tag{2}$$

where θ is the fractional coverage and κ is a constant.

The rate of desorption of a given species for first-order desorption is

$$\frac{-\mathrm{d}\theta}{\mathrm{d}t} = k\theta, \tag{3}$$

where t is the time in s and k is the first-order desorption rate constant.

From Eq. (2)

$$\theta = \frac{\mathrm{Abs}}{\kappa},$$

$$\frac{-1}{\kappa}\frac{\mathrm{d(Abs)}}{\mathrm{d}t} = \frac{k}{\kappa}\mathrm{Abs} \tag{4}$$

or

$$\frac{-\mathrm{dAbs}}{\mathrm{Abs}} = k\,\mathrm{d}t \tag{5}$$

or

$$-\mathrm{d}\ln(\mathrm{Abs}) = k\,\mathrm{d}t.$$

Integrating (5) gives

$$\ln(\mathrm{Abs}) = -kt + C, \tag{6}$$

where C is a constant.

While it is possible that some of the adsorbate will have desorbed during the 10-min He purge, the form of Eq. (6) shows that it is unnecessary to know the amount adsorbed at t_0. All that is required is a measurement of the absorbance and the time at which that absorbance was measured. The gradient of the plot of the logarithm of the absorbance against time is the desorption rate constant.

Plots of the logarithm of the absorbance of the 1600 cm^{-1} ($\ln A$) and of the 1380 cm^{-1} ($\ln B$) bands against time are shown in Figs. 5a and 5b, respectively.

The values of the desorption rate constants obtained from these are 1.72×10^{-3} (1600 cm^{-1}) and 1.76×10^{-3} (1380 cm^{-1}), the near identity of the rate constants confirming that these stretches derive from the same species.

Since we have taken the desorption to be first-order, it is totally consistent to assume a value of $10^{13}\ \mathrm{s}^{-1}$ for the desorption pre-exponential term. It is then possible to calculate the value of the desorption activation energy of the adsorbed bidentate formate species from the values of the rate constants obtained from the time dependent loss of the intensities of the absorbances of the 1600 cm^{-1} (asymmetric stretch) and of the 1380 cm^{-1} (symmetric stretch). The desorption activation energies so obtained are 127 $\mathrm{kJ\,mol}^{-1}$ for both.

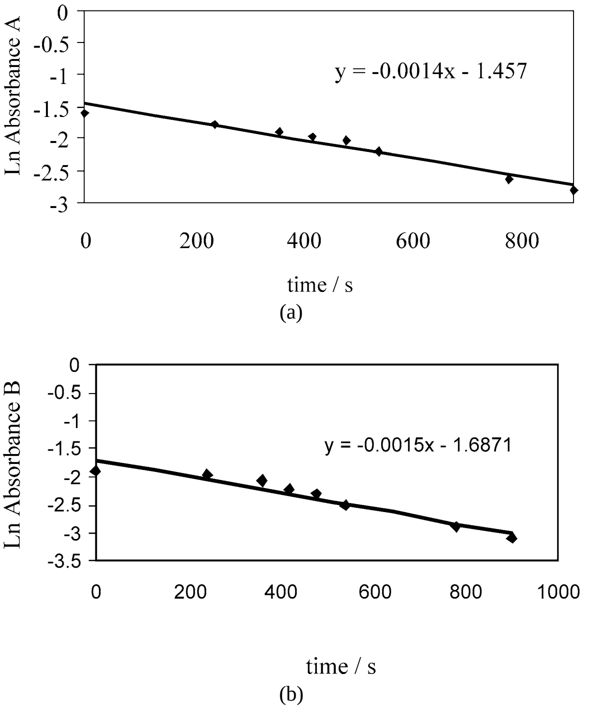

Fig. 5. (a) A plot of the natural logarithm of the absorbance of the asymmetric OCO stretch (1600 cm^{-1}) of the adsorbed formate ($\ln A$) against time. (b) A plot of the natural logarithm of the absorbance of the symmetric OCO stretch (1380 cm^{-1}) of the adsorbed formate ($\ln B$) against time.

The use of $10^{13}\ \mathrm{s}^{-1}$ for the desorption pre-exponential term derives from unimolecular reaction theory. The value of $10^{13}\ \mathrm{s}^{-1}$ is characteristic of the vibrational frequency of the bond holding adsorbates to surfaces. The model being applied then is that the adsorbate will desorb on each vibration that the requisite desorption activation energy resides (in this case 127 $\mathrm{kJ\,mol}^{-1}$) in that bond. The energy for desorption is transmitted to that critical bond from the other vibrations of the surrounding atoms. The probability of the energy being transmitted to that bond is given by the energy disadvantage term $e^{-E_\mathrm{d}/RT}$, where E_d is the desorption activation energy.

Fig. 6 is the desorption peak shape obtained by calculating the rate of desorption by integrating Eq. (3) for the following input parameters:

Pre-exponential term = $10^{13}\ \mathrm{s}^{-1}$

Desorption activation energy = 127 $\mathrm{kJ\,mol}^{-1}$

Heating rate = 10 $\mathrm{K\,min}^{-1}$

Initial surface coverage = 9×10^{14} species cm^{-2}.

The rate of desorption maximizes at 440 K, which is exactly equal to the result obtained in the temperature-programmed desorption experiment shown in Fig. 1. The peak maximum of 440 K is obtained by integration of Eq. (3) using extremely small time steps. At the end of the initial time step, calculation is made of (i) the new temperature, (ii) the rate constant for desorption, (iii) the rate of desorption, and (iv) the amount of material desorbed. (This is the product of the rate of desorption and the time interval.) This is done for the specified heating rate, the desorption activation energy, and initial value of the coverage. The new value of the coverage at the start of the second step is the initial value minus the amount desorbed in the first step. This is repeated at the end of each integration time step so that, while the rate constant, k, continues to increase

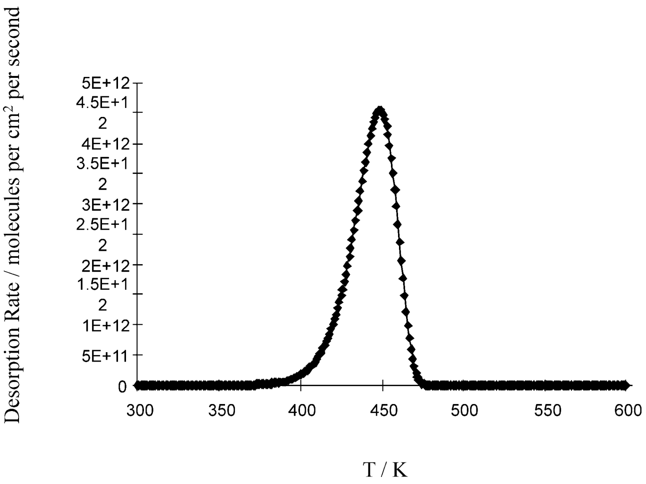

Fig. 6. Simulated temperature-programmed desorption peak shape for a desorption activation energy of 127 $\mathrm{kJ\,mol}^{-1}$, an initial coverage of 9×10^{14} species cm^{-1}, and a heating rate of 10 $\mathrm{K\,min}^{-1}$.

exponentially with increasing temperature, the product of the increasing rate constant, k, and of an exponentially decreasing coverage, θ, produced the 440 K maximum. After the maximum, this product decreases to zero as θ tends to zero.

This result confirms the validity of our earlier conclusion that the peak at 440 K of coincidentally desorbing CO_2 and H_2 derived from the decomposition of an adsorbed bidentate formate (1). It also confirms the validity assumptions used in the calculation: (i) that the desorption is first-order and (ii) that the value of $10^{13}\ s^{-1}$ used for the desorption pre-exponential term is applicable.

4. Conclusions

(1) The method of monitoring the decay with time of the intensity of a given infrared band at a fixed temperature is a valid technique for the determination of the desorption rate constant of a specified adsorbate at that temperature. The method is applicable only to first-order desorption. The desorption activation energy can be obtained from the value of the desorption rate constant at the given temperature by assuming a value of $10^{13}\ s^{-1}$ for the desorption pre-exponential term.

(2) Monitoring the decay with time of the intensity of the same infrared band isothermally at different temperatures will allow measurement of the desorption rate constant at different temperatures and hence calculation of the desorption activation energy in the absence of assuming a value for the desorption pre-exponential term.

(3) Calibrating the intensity of a given infrared band against coverage will allow the method to determine the value of the desorption rate constant of a second-order desorption process.

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