JOURNAL OF CATALYSIS 46, 275–278 (1977)

Application of an NMR Method for Measurements of Heats of Physical Adsorption

C. L. KIBBY,[1] V. YU. BOROVKOV, AND V. B. KAZANSKY

N. D. Zelinsky Institute of Organic Chemistry,
Academy of Sciences of the USSR, Moscow, U.S.S.R.

AND

W. K. HALL

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201

Received October 14, 1976

Using the Langmuir adsorption isotherm, equations were derived which connected the broadening of NMR lines with the equilibrium pressure of the adsorbate. Using NMR data on ethylene adsorption on the surface of silica–alumina, the equilibrium constants for several temperatures were calculated and the heat of physical adsorption determined. These values were almost coincident with those obtained from volumetric adsorption measurements.

INTRODUCTION

It was shown previously (*1–3*), that, if fast exchange takes place among different forms of adsorbed molecules, an NMR method was a convenient tool for investigation of complex formation on solid surfaces. Thus, measurements of the dependence of NMR spectral parameters (broadening and chemical shifts of the lines) on the surface coverage at different temperatures allow, if the complexes are not too strong, a determination of the heats and equilibrium constants for complex formation. In the case of "stable" complexes (*2*), however, it is impossible to obtain these values because the number of surface complexes is determined only by the number of active sites and is essentially independent of temperature. Nevertheless, in this case the temperature dependence of the NMR spectral parameters for the adsorbed molecules enables us to calculate the heats of physical adsorption. In this report, data on the adsorption of ethylene on silica–alumina, containing 3 wt% Al, are presented and the heat of physical adsorption is determined from the dependence of NMR linewidth on the temperature.

EXPERIMENTAL METHODS

The silica–alumina was prepared by hydrolyzing tetraethoxysilane in an acidic solution containing aluminum nitrate, then adjusting the pH with ammonium hydroxide until a gel formed (about pH 6). The gel was washed with distilled water, dried at 120°C, then calcined in air at 650°C for several hours. Before adsorption measurements were made, the silica–alumina samples were dehydrated at 500°C for 2–3 hr at 10^{-4} Torr (1 Torr = 133.3 N m^{-2})

---

[1] Present address: Pittsburgh Energy Research Center, U. S. Energy Research & Development Administration, 4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213.

ISSN 0021-9517

TABLE 1

Ethylene on Silica–Alumina[a]

Equilibrium pressure (Torr)	Temp (°C)	No. of adsorbed C_2H_4 molecules ($\times 10^{-19}$)	ΔH (Hz)
9.49	−54	3.58	200
10.35	−45	2.99	250
11.70	−36	2.41	306
12.35	−25	1.63	400
13.20	−15	1.04	560
12.28	−25	1.67	420
19.27	−25	2.30	300
32	−25	2.91	250
78	−25	3.58	210
130	−25	4.05	190
114	−54	4.67	170

[a] Variation of NMR linewidth and coverage with pressure.

pressure and kept in vacuum until exposed to ethylene. Volumetric measurements of ethylene adsorption were made simultaneously with NMR linewidth measurements. A Soviet made 60 MHz NMR spectrometer was used; details of the method and apparatus were given in Ref. (*2*).

RESULTS AND DISCUSSION

In the temperature range −54 to −15°C, the proton NMR spectrum of ethylene adsorbed on silica–alumina consisted of one line which varied in width depending on the surface coverage. The data on ethylene adsorption are listed in Table 1.

Analysis of these data shows that the linewidth depends on the amount of ethylene adsorbed; the linewidth does not depend on the temperature of the measurement.

Figure 1 shows the linear relation between the NMR linewidth of adsorbed ethylene and the inverse of the amount adsorbed. This indicates the formation of "stable" complexes of ethylene with active surface sites (*2*). In this situation, as was shown (*3*, *4*),

$$\Delta H = N_{\mathrm{ph}}\Delta H_{\mathrm{ph}} + N_c\Delta H_c, \qquad (1)$$

or,

$$\Delta H = \Delta H_{\mathrm{ph}} + N_c(H_c - \Delta H_{\mathrm{ph}}), \qquad (2)$$

where ΔH is the observed NMR linewidth; ΔH_{ph}, ΔH_c are the NMR linewidths of physically adsorbed and coordinated (complexed) molecules, respectively; N_{ph}, N_c are the mole fractions of physically adsorbed and coordinated molecules.

Since $N_c = n/V$, where n is the number of active surface sites and V is the total number of adsorbed molecules ($V \gg n$), then

$$\Delta H = \Delta H_{\mathrm{ph}} + \frac{n}{V}(\Delta H_c - \Delta H_{\mathrm{ph}}). \qquad (3)$$

From Fig. 1 it follows that the value of ΔH_{ph} is about 40 Hz.

Let us consider the adsorption measurements. In the range of temperature tested, the ethylene adsorption isotherm has the Langmuir form (Fig. 2),

$$\frac{1}{V} = \frac{1}{V_m} + \frac{1}{V_m K_p}\left(\frac{1}{P}\right), \qquad (4)$$

where V_m is the total number of adsorption

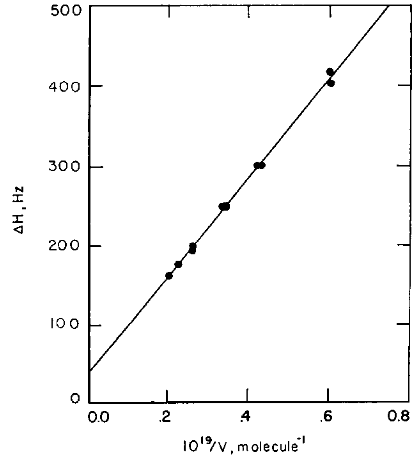

FIG. 1. Variation of linewidth with coverage. Ethylene on silica–alumina (3% Al) at −54 to −15°C.

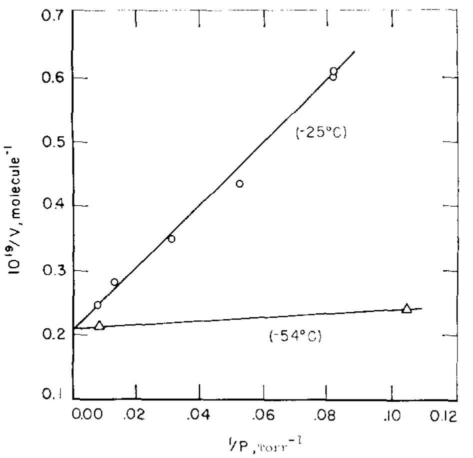

FIG. 2. Variation of reciprocal coverage with reciprocal pressure. Ethylene on silica–alumina; (⊙) at −25°C; (△) at −54°C.

sites; K_p is the equilibrium constant for physical adsorption, in pressure units; P is the equilibrium pressure of ethylene in the system.

From Eqs. (3) and (4) it follows that,

$$\Delta H = \Delta H_{\text{ph}} + \frac{n(\Delta H_c - \Delta H_{\text{ph}})}{V_m} + \frac{n(\Delta H_c - \Delta H_{\text{ph}})}{V_m K_p P}, \quad (5)$$

or,

$$\Delta\Delta H = \Delta H_h + \frac{\Delta H_h}{K_p}\left(\frac{1}{P}\right), \quad (6)$$

where $\Delta\Delta H = \Delta H - \Delta H_{\text{ph}}$ is the line broadening; $\Delta H_h = n(\Delta H_c - \Delta H_{\text{ph}})/V_m$ is the high pressure limit for the line width.

Thus, in accord with Eq. (6), the NMR line broadening should be linearly dependent on the inverse of the equilibrium pressure in the system. Such a dependence was found, as represented by Fig. 3. From the data, the value of ΔH_h is about 125 Hz. Since ΔH_c and ΔH_{ph} are independent of temperature, ΔH_h is also temperature independent.

Knowing the value of ΔH_h, it is possible to calculate the adsorption equilibrium constants, K_p, from the variation of NMR linewidth with equilibrium pressure according to Eq. (6). In Table 2, the values of K_p for ethylene on silica–alumina calculated in this way are compared to those calculated using the volumetric data and Eq. (4). Least squares fit of the two sets of data give,

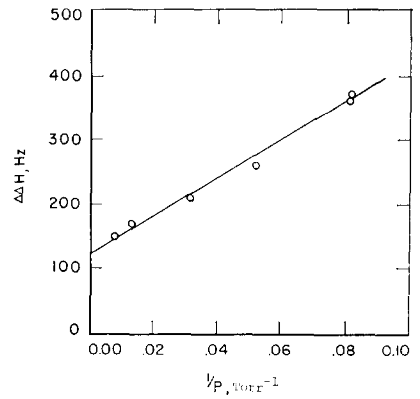

FIG. 3. Variation of line broadening with reciprocal pressure. Ethylene on silica–alumina at −25°C.

$$K_p = (4.2 \pm 0.8) \times 10^{-8}\ \text{Torr}^{-1} \times \exp(6800/RT), \quad \text{by NMR;}$$

$$K_p = (4.4 \pm 0.6) \times 10^{-8}\ \text{Torr}^{-1} \times \exp(6770/RT), \quad \text{volumetric.}$$

The coincidence of the equilibrium constants calculated by the two methods is in agreement with the suggested model of fast exchange between adsorbed and coordi-

TABLE 2

Ethylene on Silica-Alumina[a]

T (°C)	ln (K_p, Torr^{-1})		Difference
	NMR	Volumetric	
−54	−1.007	−1.241	+0.234
−45	−1.958	−1.910	−0.048
−36	−2.590	−2.501	−0.089
−25	−3.146	−3.218	+0.072
−15	−3.729	−3.863	+0.134
−25	−3.218	−3.170	−0.048
−25	−3.036	−3.079	+0.043
−25	−3.090	−3.079	−0.011
−25	−3.352	−3.352	0
−25	−3.296	−3.296	0
−54	−1.742	−1.682	−0.060
−25	−3.19 (mean)	−3.20 (mean)	0.01
−54	−1.37 (mean)	−1.46 (mean)	0.09

[a] Adsorption equilibrium constants from NMR and volumetric methods.

nated molecules (*1*, *3*). It demonstrates that NMR can be applied successfully to the determination of heats of physical adsorption, especially when direct volumetric measurements are restricted, for example, in the case of adsorption at high pressures or from liquid solutions.

ACKNOWLEDGMENT

The authors thank the Academy of Sciences of the USSR and the U. S. National Science Foundation (grant No. CHE73-08978 A02), whose joint support of the US-USSR exchange program in catalysis made this work possible. One of the authors (C. L. K.) is particularly grateful to Gulf Research & Development Co. for a leave of absence, to the American Chemical Society and U. S. Department of State, administrators of the program on the U. S. side, and to all of the workers at the N. D. Zelinsky Institute of Organic Chemistry who were so helpful to him during his stay there.

REFERENCES

1. Borovkov, V. Y. and Kazansky, V. B., *Kinet. Katal.* **13**, 1356; 1372 (1972).

2. Kazansky, V. B., Borovkov, V. Y., and Zhidimirov, G. M., *J. Catal.* **39**, 205 (1957).

3. Borovkov, V. Y., and Kazansky, V. B., *Kinet. Katal.* **15**, 705 (1974).

4. Borovkov, V. Y., Zhidimirov, G. B., and Kazansky, V. B., *Zh. Strukt. Khim.* **16**, 308 (1975).