

acidity, at least at temperatures up to 300°C, that is strong enough to protonate pyridine. One might argue that the number of protonic sites was too low to be detected. The number of active sites for the cyclohexene isomerization, which could have been interpreted by means of a proton addition, has been measured recently by pyridine poisoning (12) and found to be sufficiently high (2 to 4 per 1000 Å²) to be easily detectable by ir-spectroscopy. It thus seems that protonic sites on alumina cannot act as active sites in hydrocarbon reactions at temperatures below 300°C, since most reactants such as alkanes or alkenes have much lower basicities than pyridine.

REFERENCES

1. PARRY, E. P., *J. Catal.* **2**, 371 (1963).
2. BASILA, M. R., KANTNER, T. R., AND RHEE, K. H., *J. Phys. Chem.* **68**, 3197 (1964).
3. PICHAT, P., MATHIEU, M.-V., AND IMELIK, B., *Bull. Soc. Chim.* **1969**, 2611.

4. KNÖZINGER, H., AND STOLZ, H., *Fortschr. Koll. Polym.* **55**, 16 (1971).
5. PERI, J. B., *J. Phys. Chem.* **69**, 231 (1965).
6. DUNKEN, H., FINK, P., AND PILZ, E., *Chem. Technik.* **18**, 490 (1966).
7. PINES, H., AND HAAG, W. O., *J. Amer. Chem. Soc.* **82**, 2471 (1960).
8. KNÖZINGER, H., AND SCHEGLILA, A., *J. Catal.* **17**, 252 (1970).
9. WARD, J. W., *J. Catal.* **11**, 259 (1968).
10. KNÖZINGER, H., STOLZ, H., BÜHL, H., CLEMENT, G., AND MEYE, W., *Chemie Ing.-Techn.* **42**, 548 (1970).
11. BASSET, J., MATHIEU, M.-V., AND PRETTRE, M., *Rev. Chim. Minéral.* **5**, 945 (1968); and *J. Chim. Phys.* **66**, 611 (1969).
12. GÁTI, GY., AND KNÖZINGER, H., *Z. phys. Chem. (Frankfurt)*, in press.

HELMUT KNÖZINGER

CARSTEN - PETER KAERLEIN

*Physikalisch-Chemisches Institut
Universität München
Sophienstr. 11
8 München 2, Germany
Received August 28, 1971*

Chemisorption of Methanol and Electrical Conductivity Changes on Vanadium Pentoxide Catalysts

Vanadium pentoxide prepared by the decomposition of vanadyl oxalate (catalyst I) has a greater catalytic activity than that prepared by the decomposition of ammonium metavanadate (catalyst II) (1-3). Recently we have reported (4, 5) that catalyst I possesses more surface area, larger magnetic susceptibility and a greater concentration of V⁴⁺ ions than catalyst II and also a greater amount of oxygen becomes chemisorbed on catalyst I at a faster rate. The kinetics of chemisorption of methanol and the accompanying electrical conductivity changes on catalysts (I and II) have now been studied.

Catalyst I was prepared by the decomposition of vanadyl oxalate at 400°C for 4 hr in a continuous stream of air.

Catalyst II was prepared by the decomposition of ammonium metavanadate at 400°C for 4 hr in a continuous stream of air. Chemisorption was studied in a conventional volumetric adsorption apparatus. The amount adsorbed was directly represented by the drop in pressure (Δp) in a constant volume system, without converting it to volume. The measurements were carried out by taking 10 g of powdered catalyst at an initial methanol pressure of 14 cm in the temperature range, 35-200°C. Absolute methanol, further purified and freed from moisture by distillation over magnesium metal, was used. To monitor electrical conductivity, the resistance of a pelleted sample was measured in the temperature range, 70-200°C, by an electronic dc voltmeter; details of the method

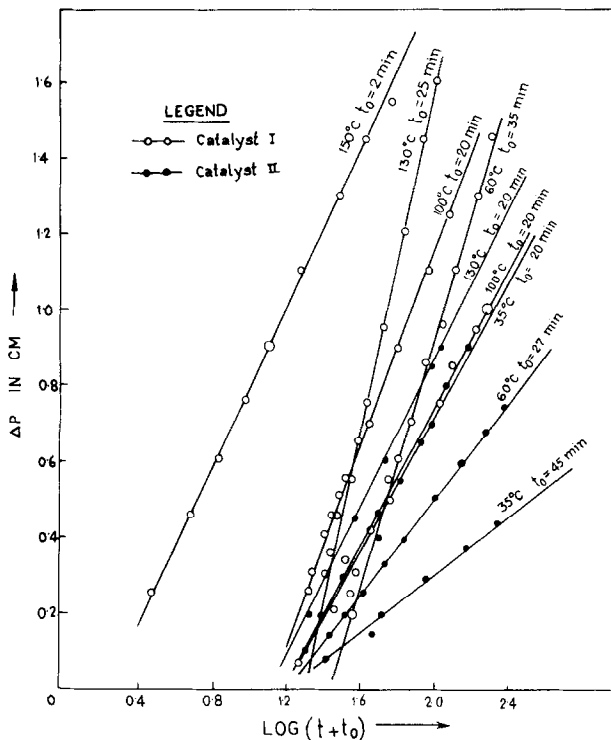


FIGURE 1

and procedure were given in an earlier paper (6). The degassing was done at 520°C for 8 hr.

Kinetics of chemisorption of methanol were studied at 35, 60, 100, 175, and 200°C on vanadium pentoxide catalysts (I and II). Figure 1 shows the plots of Δp against $\log(t + t_0)$ according to the Elovich equation,

$$q = \frac{2.303}{\alpha} \log(t + t_0) - \frac{2.303}{\alpha} \log t_0 + q_0,$$

where a is the rate of initial uptake and α is the Elovich constant denoting the deceleration of the process, respectively; t_0 is an arbitrary constant determined by trial and error to linearize the Elovich plots, $a = 1/(at_0)$, q is the amount of gas adsorbed in time t , and q_0 is the amount of gas adsorbed by a very fast process preceding the slow chemisorption. The values of the Elovich parameters α , a , and t_0 are given in Table 1. Figure 2 shows the variation of α with temperature.

TABLE 1
ELOVICH CONSTANTS FOR METHANOL CHEMISORPTION ON VANADIUM PENTOXIDE CATALYSTS

Temp (°C)	Catalyst I				Catalyst II			
	α (cm ⁻¹ g)	$a \times 10^3$ (cm g ⁻¹ min ⁻¹)	$q_0 \times 10^2$ (cm g ⁻¹)	t_0 (min)	α (cm ⁻¹ g)	$a \times 10^3$ (cm g ⁻¹ min ⁻¹)	$q \times 10^2$ (cm g ⁻¹)	t_0 (min)
35	25.3	1.97	0	20.0	50.8	0.437	0	45.0
60	14.3	1.99	2.63	35.0	35.0	1.05	0	27.0
100	18.0	2.78	1.70	20.0	25.5	1.96	0	20.0
130	10.3	4.85	5.41	25.0	23.4	2.13	1.10	20.0

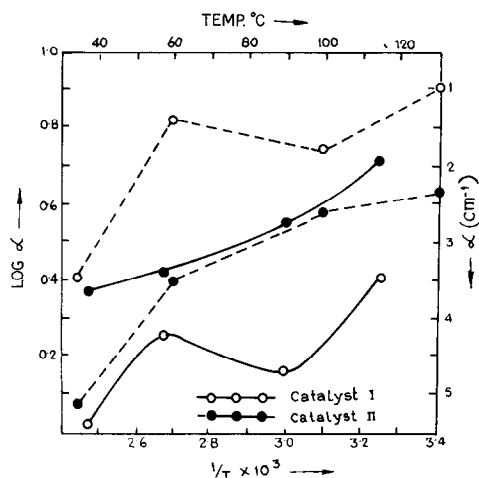


FIG. 2. (—) $\log \alpha$ vs $1/T$; (---) α vs temperature.

The conductivity measurements during methanol chemisorption were carried out at 70, 100, 120, 140, and 200°C by adding a certain amount of methanol vapor to the system and noting the equilibrium electrical conductivity. The conductivity increases with methanol chemisorption and the percentage increases in conductivity ($\Delta C/C$)% are plotted against temperature at a constant pressure in Fig. 3.

A survey of the results on the kinetics of methanol chemisorption and of electrical

conductivity changes on the two vanadium pentoxide catalysts (I and II) shows that different types of chemisorption of methanol vapor occur at different temperatures. Thus, plots of the Elovich constant α vs temperature (Fig. 2) show breaks around 60°C in the temperature range, 35–130°C. The low temperature chemisorption proceeds without any electron transfer between the catalysts and the methanol molecules, as there is no change in electrical conductivity of catalyst I below 70°C and of catalyst II below 100°C (Fig. 3).

The data on the kinetics of methanol chemisorption (Table 1) further reveal that the catalyst I is characterized by greater chemisorption of methanol vapor. Here not only the total amount of methanol chemisorbed, but also the rate of methanol chemisorption are found to be more. At higher temperatures, the increase in conductivity produced by the chemisorption of methanol is found to be greater for catalyst I (Fig. 3).

It has been observed by the authors earlier (4, 5) that catalyst I has a larger surface area (10 m²/g) than catalyst II (8.5 m²/g). Moreover, studies on oxygen chemisorption and accompanying electrical conductivity changes along with chemical

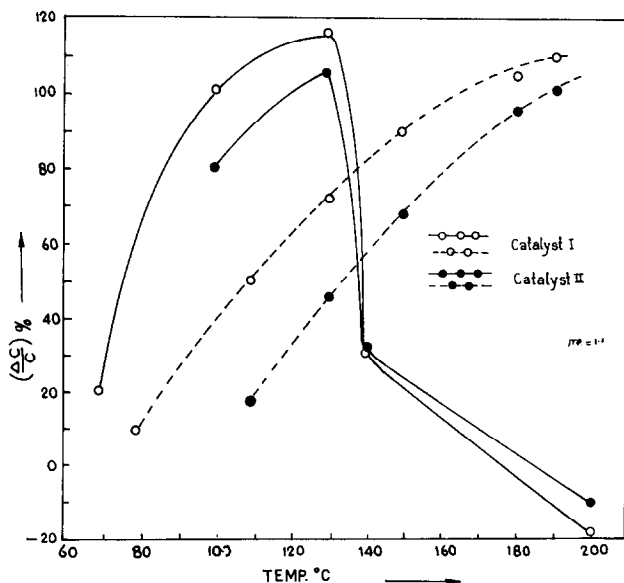


FIG. 3 (—) pressure = 8 cm (static method); (---) pressure = 1.5 cm (flow method).

analysis indicate a greater concentration of anion vacancies and free electrons in catalyst I than in catalyst II. The concentration of V^{4+} ions in catalyst I is 2% while that in catalyst II is 1%. These V^{4+} ions may play some part in methanol chemisorption but the nature of this is difficult to define.

REFERENCES

1. BHATTACHARYYA, S. K., AND GULATI, I. B., *Ind. Eng. Chem.* **50**, 1719 (1958).
2. BHATTACHARYYA, S. K., AND VENKATRAMAN, N., *J. Appl. Chem.* **8**, 728, 735 (1958).
3. BHATTACHARYYA, S. K., AND GANGULI, N. D., *J. Indian Chem. Soc.* **38**, 463 (1961).
4. BHATTACHARYYA, S. K., AND MAHANTI, P., *Proc.*

Int. Congr. Catal., 4th, Moscow, pap. No. 1, 23 (1968).

5. BHATTACHARYYA, S. K., AND MAHANTI, P., *J. Catal.* **12**, 20 (1971).
6. BHATTACHARYYA, S. K., DE, K. S., PANDAO, S. N., AND CHANDRASEKHAR, G. V., *Proc. Int. Congr. Catal.*, 3rd, 1964, 474 (1965).

S. K. BHATTACHARYYA
P. MAHANTI

*Department of Chemistry,
Banaras Hindu University,
Varanasi-5, India**; and
*Indian Institute of Technology,
Kharagpur, India
Received May 19, 1971*

* Present address.

Pressure Effects on the Elovich Kinetics*

INTRODUCTION

In the earlier paper (1), kinetics of hydrogen chemisorption on nickel-alumina catalysts were analyzed using the Elovich equation, viz.,

$$dq/dt = a \cdot \exp(-\alpha q) \quad (1)$$

where q is the amount of gas adsorbed at time t , and a and α are constants, and a detailed study of the influence of temperature and initial pressure on the Elovich parameters was made. The present note deals with the effect of prevailing gas pressure on the rate of hydrogen chemisorption on nickel-alumina catalyst. Before doing experiments involving changes in the prevailing gas pressure, the catalyst was studied for its general adsorption behavior for the parameters a and α , and for the reproducibility of the surface at different temperatures and initial pressures (1).

EXPERIMENTAL

Adsorption measurements were carried out in a constant volume adsorption sys-

tem, provided with a McLeod gauge and accurately calibrated mercury manometers. The nickel-alumina catalyst used in this study is the same "Catalyst 2" reported earlier (1) with a BET surface area of 118 m²/g, and a metal surface area of 12.09 m²/g.

Purification of gases, dead space determination, and the general kinetics experiments were carried out following the procedure described earlier (1). Changes in the prevailing gas pressures were brought about at the time t_c , after the onset of slow adsorption (i) by addition, (ii) by removal of a certain quantity of gas, keeping the volume of the system constant, and (iii) by cutting off a certain volume of the adsorption system during adsorption.

RESULTS AND DISCUSSION

Effect of Initial Pressure

The effect of initial pressure on the Elovich parameters was studied at 30 and 200°C and the results are plotted in Fig. 1. Both α_1 and α_2 , the α values for the kinetics stages 1 and 2, respectively, in-

* This work was done at the Chemistry Department of Loyola College, Madras 34, India.