JOURNAL OF CATALYSIS 87, 520–523 (1984)

Oxygen Chemisorption on V_2O_5

Isotherms and Isobars of Adsorption

INTRODUCTION

V_2O_5 is a semiconductor oxide largely used as catalyst in reactions of hydrocarbon partial oxidation, either pure or mixed with other substances such as TiO_2, SiO_2, SO_4K_2, etc.

Generally, it has been accepted that the hydrocarbon oxidation with V_2O_5 involves a series of steps, among them, the adsorption of the hydrocarbon molecule, its reaction with the adsorbed or surface oxygen of the system and the reaction products desorption. In this way, an oxygen vacancy is produced which afterward is combined with oxygen from the gas phase. Consequently, V_2O_5 capacity to adsorb oxygen from the gas phase and/or exchange it with that of the system, is a fundamental parameter connected with this kind of lower area catalyst (*1–6*).

In its normal state, V_2O_5 is a nonstoichiometric oxide that shows oxygen vacancies with the subsequent formation of V^{4+} ions (*7*).

The aim of the present work is to report experimental results of oxygen adsorption on V_2O_5 (isotherms and isobars). These results allow to develop an interaction model between oxygen (gaseous, adsorbed, and bulk) and solid phase (V_2O_5).

EXPERIMENTAL

V_2O_5 was obtained by the precipitation from an hydrochloric solution of ammonium vanadate neutralizing the initial solution with NH_4OH to pH 7.

After this, the sample was dried at 120°C, ground and burned at 550°C during 24 h in air.

The specific surface of the sample was measured using the BET method by N_2 physisorption in a Micromeritics Accusorb apparatus. The obtained surface, 2.6 m^2/g, was the average of 3 measurements.

The adsorption isotherms were measured in a conventional volumetric apparatus made of Pyrex glass, with a silica-glass reactor (to avoid bronze formation). Greaseless stopcocks were used in its construction.

The pressure was measured by a termistor. Previously it was calibrated with N_2 for volume calibration and with O_2 for adsorption, against MacLeod absolute manometer, under a pressure range of 10^{-3}–2 Torr (1 Torr = 133,3 N m^{-2}).

The pressure measure was corrected by the Apparent Volume method (*9*) to avoid the thermal transpiration effect.

The termistor capsule was placed into an air thermostatic bath to minimize the ambient temperature fluctuation.

Each isotherm was repeated at least one more time. The differences between the measurements were lower than 15%.

The sample ($\simeq$300 mg) was ground (0–36 μm) and spread along the reactor (~5 cm), to minimize the diffusional effects among the particles.

The surface stabilization of oxides of the transition metals is extremely important in adsorption experiments. Due to the fact that V_2O_5 has a tendency to lose oxygen easily, the sample must be standardized prior to each isotherm determination. The standard sample is obtained heating under high vacuum (reducing conditions) and O_2 atmosphere (oxidizing conditions) in order to reach the reversibility range.

0021-9517/84 $3.00

These conditions (vacuum and temperature) should (1) allow the greatest extraction of adsorbed oxygen, and (2) not be so extreme as to change the crystalline structure of the sample.

So, the conditions in which the sample must be treated to reach the reversibility previously cited, were studied with a Cahn R. G. microbalance with a sensibility of 10^{-7} g. Different temperatures, evacuation times, and treatments with oxygen were proved.

The results showed that, by repeating this pretreatment seven times (1 at. O_2 at 500°C for 1 h, and later evacuation to 10^{-6} Torr during 45 minutes) the reversibility was obtained. The evacuation pressure was controlled with the MacLeod manometer.

The reversibility consists of reaching the constancy of the oxygen amount that sample loses or gains among the treatments previously cited. This constant amount is reached after the seventh time. Perhaps, it occurs because the sample suffers an effect of loss of surface or a rearrangement of crystalline planes.

Figure 1 shows the change of the sample weight versus the number of the treatments.

In the sample treated 13 times the equilibrium was quenched at 500°C and 10^{-6} Torr. Then, it was studied by X-ray diffractometry. In this way, the constancy of the initial crystalline structure was confirmed.

The crystals size of either original or pretreatment samples was greater than the crystals size detection limit of the X-ray diffractometer methods.

After the sample was evacuated seven times at 500°C (pretreatment) the reactor temperature was decreased at isotherms temperature. The system reached the pressure equilibrium (P_e). Then determined amounts of oxygen were successively added to measure the successive adsorption isotherm points.

Before each new isotherm, a pretreatment step was made on the same sample.

RESULTS AND DISCUSSION

Figure 2 shows oxygen adsorption isotherms on V_2O_5 within the temperature range of 100–450°C, and for values of P between 10^{-3} and 2 Torr, where P is the equilibrium pressure for each isotherm point.

Experimental values, obtained at 0°C showed that the amount of adsorbed oxygen was not significant.

The isotherms showed that the amount of adsorbed oxygen is very small, at all pressure ranges. The maximum value of coverage was $\theta_{250°C} = 0{,}015$. The low-temperature isotherms, in which only the adsorption process exists, were fitted to the models of Temkin, Freundlich, and Langmuir. The best fit was achieved following Langmuir's model. It is expressed mathematically as

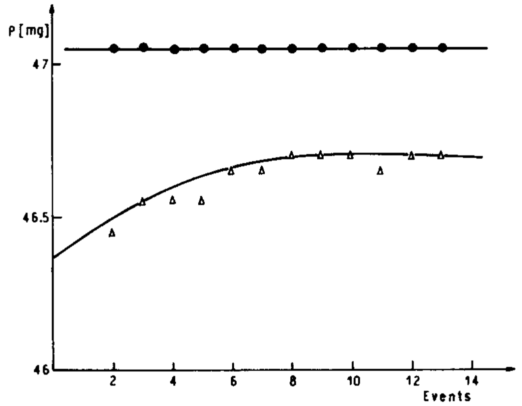

FIG. 1. Weight sample change treatments number; ●, 500°C, 1 atm O_2; △, 500°C, 10^{-6} Torr.

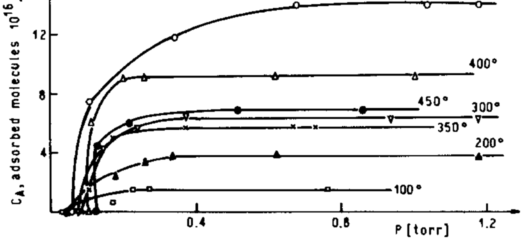

FIG. 2. Adsorption isotherms for oxygen on vanadium pentoxide.

$$C_a = \frac{K(P - P_e)}{1 + K'(P - P_e)} \qquad (1)$$

where K and K', constants; C_a, number of adsorbed molecules; P_e, initial equilibrium pressure.

P_e is considered as the first equilibrium pressure that is reached at the temperature of each isotherm in the reactor at the beginning of it, after the seventh evacuation at 500°C (pretreatment).

The use of the term $(P - P_e)$ in the expression (*1*) is justified because C_a value must be zero when $P = P_e$, and the last ones are of the same magnitude order.

The parameters obtained from this fitting can be observed in Table 1. Bielanski *et al.* (*10*) measured the isobars of the V_2O_5–MoO_3 and pure system V_2O_5 within the temperature range of 20 to 350°C and pressures of 10^{-2} Torr. V_2O_5 isobar presents its maximum at 170°C, displaced to lower temperatures according to our data (Fig. 3) but in a similar way. This may be due to a different pretreatment of the samples.

In order to improve the analysis of the results, the isobar can be divided into two temperature ranges:

(a) Range 0–300°C. In this range, the isobar shows a maximum at 250°C. The superficial V^{4+} oxidation to V^{5+} with O^{2-} formation as an adsorbed phase is proposed. This adsorption model may be suggested in accordance to the experimental data of O_2 adsorption on V_2O_5 provided by Bielanski (*11*) and Dyrek (*7*). Bielanski found that during the adsorption, at 200°C, there is no bulk interaction with the O_2 atmosphere and that it only starts at 300°C but as a very slow process. Dyrek determined by means of EPR that chemisorption of oxygen at temperatures between 250 and 350°C leads to a relatively low coverage of the surface with the formation of diamagnetic O^{2-} ions. Besides, Bhattacharyya (*4*) found that during the chemisorption of oxygen between 120 and 400°C only one type of chemisorbed oxygen is formed on the surface.

TABLE 1

Adjusting Parameters as They Appear in the Langmuir Adsorption Model

	T (°C)			
	100	200	250	300
K(molec/Torr)	1.66×10^{14}	7.17×10^{14}	1.61×10^{15}	7.83×10^{14}
K′(1/Torr)	8.73×10^{-3}	1.81×10^{-2}	1.07×10^{-2}	1.11×10^{-2}
Correlations	0.9343	0.9978	0.9991	0.9986

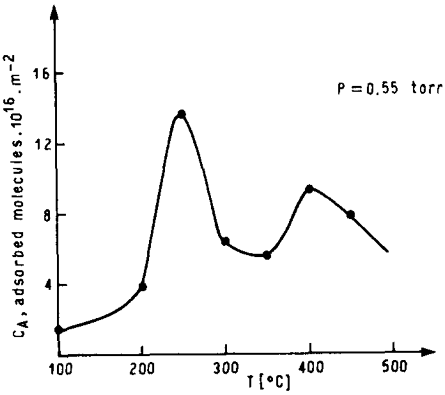

FIG. 3. Adsorption isobar for oxygen on vanadium pentoxide.

(b) Range 300–450°C. In this temperature range, the diffusional phenomenon appears together with that of the chemisorption as it can be deduced with the presence of a minimum (at $T \simeq 350°C$) and then, a maximum (at $T \simeq 400°C$) in the isobar.

At temperatures higher than 300°C, the uptake of oxygen follows a square root of time or parabolic rate law (Fig. 4). This behavior appears where diffusional processes are involved and might be due to the laminar shape of V_2O_5 crystallites. Similar results were obtained by Bielanski (*11*) and Simard (*1*).

Furthermore, the necessary time to reach the equilibrium for each point of the isotherms, have confirmed the diffusional mechanism in this adsorption process. Thus, higher times are obtained at 300°C than at the other temperatures (100, 200, 350, 400, and 450°C) comparatively.

The Tamman temperature for V_2O_5 is 200°C and, the structure is extremely open,

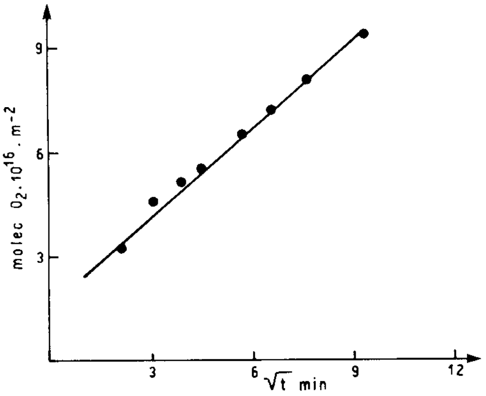

FIG. 4. Linear dependence to the amount of oxygen chemisorbed at 400°C as a function of time.

with some oxygen defects in the system. So, it can be supposed that the mobility of the O^{2-} ions is large enough to allow them to migrate to the bulk phase, consequently the oxygen vacancies migrate toward the surface too. This is the controlling mechanism for the oxygen adsorption within the range of 300–400°C. At higher temperatures (400–450°C) the adsorption controls the whole process again.

These results may be interesting from a catalytic point of view since all the industrial processes in which V_2O_5 is used as catalyst are at temperatures higher than 300°C. So, any modification of the bulk properties must affect its catalytic properties.

REFERENCES

1. Simard, G. L., Steger, J. F. Arnott, R. T., and Siegel, L. A., *Ind. Eng. Chem.* **47,** 1424 (1955).
2. Stanislaus, A., Evans, M. J. B., and Mann, R. F., *Canad. J. Chem. Eng.* **51,** 725 (1973).
3. Grzybowska, B., Barbaux, Y., and Bonnelle, J. P., *J. Chem. Res. Synop.* **48**(M), 0556 (1981).
4. Bhattacharyya, S. K., and Mahanti, P., *J. Catal.* **20,** 10 (1971).
5. Gonzalez-Cruz, L., Joly, J. P., and Germain, J. E., *J. Chem. Phys.* **75,** 324 (1978).
6. Kera, Y., and Hirota, K. J., *Phys. Chem.* **73,** 3973 (1969).
7. Dyrek, K., *Bull. Acad. Pol. Sci.* **22,** 605 (1974).
8. Gambaro, L. A., Thomas, H. J., and Pereira, E., *Transition Met. Chem.* **5,** 139 (1980).
9. Gonzalez Tejuca, L., Doctoral thesis, Univ. Complutense, Madrid, Spain (1970).
10. Bielanski, A., and Dziembaj, R., *Bull. Acad. Pol. Ser. Sci. Chim.* **21,** 547 (1973).
11. Bielanski, A., Dyrek, K., and Serwicka, E., *J. Catal.* **66,** 316 (1980).
12. Vol'kenshtein, F. F., "The Electronic Theory of Catalysis on Semiconductors." Pergamon, New York, 1963.

L. REY
L. A. GAMBARO
H. J. THOMAS[1]

Centro de Investigación y Dessarrollo
en Procesos Catalíticos (CINDECA)
Calle 47 No. 257 1900 La Plata, Argentine

Received July 5, 1983

---

[1] To whom queries concerning this paper should be sent.