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A Thermodesorption Study of the System Olefin–NiO

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The system olefin–NiO has been investigated by means of a thermodesorption technique. A decrease in the temperature of desorption, $T_m{}^{I} > T_m{}^{II} > T_m{}^{III}$ was observed following the first, second, and third introduction of olefin to the NiO catalyst (at a uniform rate of the temperature rise); on further introduction of the olefin, the catalyst is "stabilized" and T_m remains constant. The energy of activation of desorption and the heats of adsorption of some olefins have been determined. Reversible chemisorption of ethylene on NiO takes place on a surface estimated to amount to 0.08–0.15% of the total surface under the various experimental conditions used. The chromatograms recorded after the third and following introductions of olefin show a peak due to reversibly chemisorbed olefin and a group of peaks due to products of irreversible chemisorption (dimers, oxygen-containing compounds, etc.).

I. INTRODUCTION

The interaction of olefins with the surface of transition metal oxides, has been investigated by several authors (*1–7*). Kubokawa *et al.* (*1*) have reported that *n*-type oxides show a greater activity in the reversible adsorption of propylene than *p*-type oxides. A study of the changes in the surface potential of oxide catalysts by Enikeev *et al.* (*5, 6*) led to the conclusion that a donor type adsorption takes place. Morooka and Ozaki (*7*) came to the conclusion that the oxidation of olefins over NiO proceeds via a π-complex intermediate which donates electrons to the surface.

The present paper reports a study of the system, olefin–NiO, by means of the thermodesorption technique. The same technique has been used by Amenomiya and Cvetanovic to investigate the system, ethylene–Al_2O_3 (*8*).

The interaction of olefins with NiO (*9–12*) was studied by the thermodesorption technique using the Polanyi-Wigner equation (*13*) to determine the rate of desorption, r_d, i.e.,

$$r_d = -v_m \frac{d\theta}{d} = k_0\, \theta \exp\left(-E_d/RT\right), \quad (1)$$

where v_m is the amount of adsorbed material at $\theta = 1$, θ is the surface coverage, E_d is the activation energy of desorption, T is the absolute temperature, t is the time and k_0 is a constant ($T = T_m$ at $dr_d/dt = 0$).

The dependence of E_d upon T_m is obtained by differentiating Eq. (1). If the temperature rises linearly with time ($T = T_0 + \beta t$) Eq. (2) follows:

$$2 \log T_m - \log \beta = \frac{E_d}{2.303RT_m} + \log \frac{E_d v_m}{Rk_0} \quad (2)$$

where T_0 is the temperature of adsorption, T_m is the temperature at which the maximum of the peak emerges, β is the rate of temperature increase (°C/min) (*8–13*).

II. EXPERIMENTAL METHODS

NiO was obtained by precipitation of $Ni(NO_3)_2$ with NH_4OH. Precipitation began at pH = 6.7–7.7 and ended at pH = 9.7. The precipitate was filtered, dried, and heated for 4 hr at 500°C. From the NiO obtained, a 30–70 mesh fraction (specific

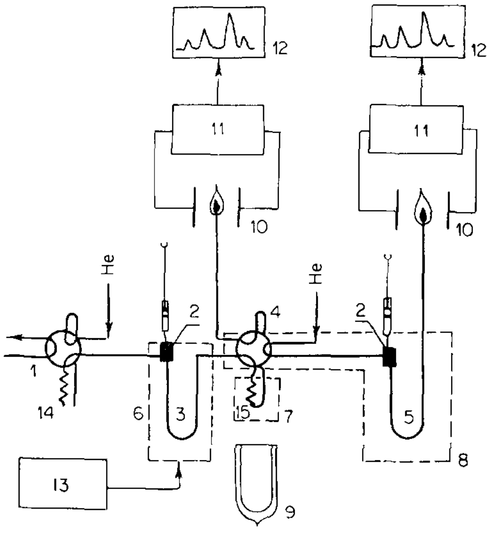

FIG. 1. Diagram of the chromatographic thermodesorption apparatus. (1,14) gas sample inlet stopcock; (2) sample injector; (3) catalyst column; (4) four-way stopcock; (5) chromatographic column; (6,7, and 8) thermostating units; (9) Dewar flask; (10) FID; (11) amplifier; (12) recorder; (13) linear temperature programming system; (15) cold trap.

surface area 30.2 m^2/g) was taken. The olefins used were of 99.97% purity (Fluka).

The apparatus used is shown in Fig. 1. Helium of high purity was used as the carrier gas. To remove traces of moisture the carrier gas was passed through a molecular sieve, 5 Å, cooled with liquid nitrogen. The gas samples were admitted to the reactor by means of a four-way stopcock provided with gas pipets of various volumes. The reactor was a U-shaped glass tube (i.d., 0.4 cm) containing 1 g of NiO with a volume of ca. 0.6 cm^3. The gas stream leaving the reactor by a four-way stopcock was admitted to the detector or to a liquid nitrogen trap, where the products of the reaction were condensed. Quick evaporation of these products was achieved with a sand bath at 200°C. Gas chromatography was carried in a column (170 cm; i.d., 0.2 cm) packed with inactivated silica gel (100–140 mesh) at a flow rate of the carrier gas of 17.5 ml/min.

The flow rate of the carrier gas in the reactor was 12.5 ml/min. With the volume of the catalyst used, the rate was sufficient to ensure that no significant readsorption takes place. Further it has been found that T_m does not vary with the changes in the gas flow rate (*8*).

Prior to each experiment the NiO packing was treated 7–8 times with ca. 20-ml portions of air at 300°C under a constant helium flow. The sample was kept at this temperature for 1 hr.

The gaseous hydrocarbons were admitted to the reactor with a gas pipet and the liquid ones with a microsyringe. The sample volume was 3 ml and 2 μliter; respectively. The hydrocarbon was injected at a catalyst temperature of 28°C. The peak of the hydrocarbon was recorded and when the recorder base line became stable again the programming controller was switched on. The temperatures at which the desorption peak maxima emerged (T_m) were determined by means of a thermocouple and a precise milivoltmeter with an accuracy of ±1°C corresponding to an error in the energy of activation of desorption of ±0.1 kcal/mole. The rate of temperature rise was programmed at 10, 15, 20, 25, and 30°C/min.

The isosteric heat of adsorption Q_a was determined by the change in the specific retention volume V_g^T with the temperature T_c from the following equation:

$$\ln \frac{V_g^T}{T_c} = \ln A + \frac{Q_a}{RT_c} \qquad (3)$$

where R is the gas constant and A is the entropy factor. For the determination of Q_a in place of the reactor a spiral column packed with 10 g of NiO was used.

III. RESULTS AND DISCUSSION

Figure 2 shows a desorption chromatogram of ethylene at a rate of temperature rise $\beta = 20°C/min$. Two desorption peaks are depicted with $T_m = 89$ and 281°C, respectively. The substances desorbing below 120°C were condensed in a liquid nitrogen trap. Subsequent chromatographic analysis showed this to be ethylene (the first peak in Fig. 2a).

Repetition of the cycle (at the same rate of temperature rise) led to a decrease of

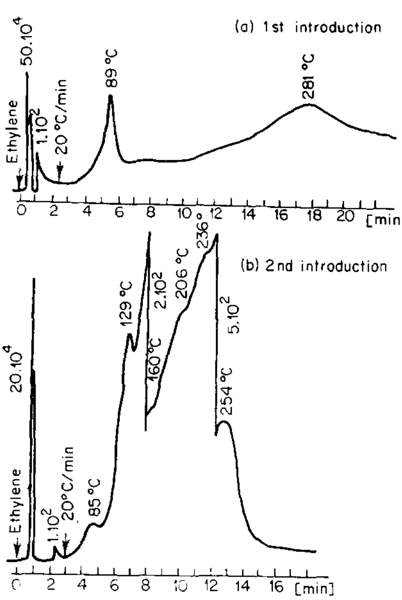

FIG. 2. Ethylene: (a) first introduction (β = 20°C/min); (b) second introduction (β = 20°C/min). The remaining numbers on Figs. 2, 3, and 4 denote the sensitivities of the instrument used.

the desorption temperature ($T_m = 85°C$, Fig. 2b). After the third introduction of ethylene the temperature of desorption decreases by further 2–3°C and then remains constant in the following experiments. The desorption chromatogram obtained after the second and following introduction of ethylene showed new peaks emerging in the interval of 130 to 260°C. These peaks are absent in the chromatogram obtained after the first introduction of ethylene (Fig. 2a). As shown in Fig. 2b the ethylene peak is partially overlapped by the second peak ($T_m = 129°C$). In the absence of the second peak the ethylene maximum probably would be shifted toward the beginning of the chromatogram; and a still lower T_m would have been obtained.

The experiments at other rates of temperature increase were carried out in the same manner and the same phenomena were observed. The data obtained for T_m at the various β afforded by means of Eq. (2) the activation energy of desorption E_d. For the first, second, and third introduction of ethylene the values obtained for E_d were, respectively, 7.8, 8.0, and 8.1 kcal/mole. The observed changes in T_m lead to insignificant changes in E_d. Usually T_m remained constant (at fixed β) after the third introduction of olefin; the catalyst became "stabilized."

The average activation energies of desorption obtained by means of Eq. (2) for the "stabilized" state of the catalyst for the several olefins are listed in Table 1. The heats of physical adsorption obtained chromatographically using Eq. (3) are also presented in Table 1.

TABLE 1
ACTIVATION ENERGY OF DESORPTION AND ISOSTERIC HEAT OF ADSORPTION

Olefin	Q_a (kcal/mole)	E_d (kcal/mole)
1. Ethylene	6.0	8.0
2. Propylene	7.2	8.2
3. *cis*-2-Butene	8.8	9.3
4. *trans*-2-Butene	8.9	10.2
5. 2-Methyl-2-butene	9.6	10.4
6. 2,3-Dimethyl-2-butene	—	12.3

The decrease of the thermodesorption temperature after the first cycle is probably due to changes in some of the active sites of the catalyst. When the first portion of hydrocarbon is admitted to the catalyst, its most active sites are blocked. This view is supported by the observation that the elemental analysis of a catalyst sample, with which several adsorptions of ethylene had been carried out, disclosed the presence of traces of carbon inspite of the fact that the sample had been treated with air at 300°C after each experiment.

As already mentioned, the desorption after the second admittance of ethylene gives rise to a group of peaks emerging in the 130–260°C temperature interval. The chromatograms obtained from the following cycles remain of practically the same appearance. The infrared spectra of the substances desorbed above 130°C (in the case of propylene adsorption) indicated the presence of hydrocarbons (2900–3000 cm^{-1}) olefinic double bond (900 cm^{-1}) and oxygen-

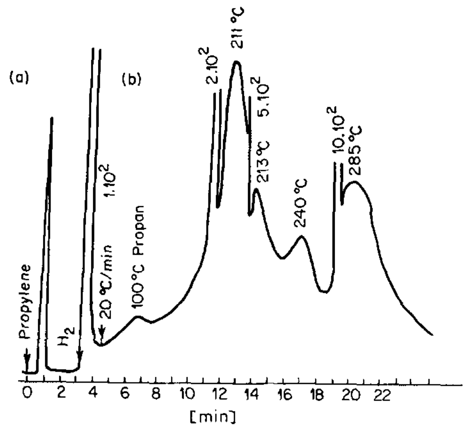

FIG. 3. Thermodesorption chromatogram of propylene; carrier gas: (a) helium, (b) hydrogen.

containing compounds (1715 and 1030 cm^{-1}). A more detailed analysis of these products and the paths of their formation are the object of further investigations. Preliminary experiments have shown that the oxide oxygen takes part in their formation.

The values of the activation energy of desorption vary between 8 and 12 kcal/mole. We assume that under the above experimental conditions the E_d-values obtained refer to a weak nondissociative chemisorption taking place on definite sites of the catalyst. It is noteworthy that the values of E_d are close in magnitude to those of the heats of physical adsorption, Q_a, for the same hydrocarbons.

In one series of experiments after admitting the olefin to the catalyst and when the base line of the recorder became stable again, the carrier gas was changed from helium to hydrogen. When the temperature programming controller was switched on (experiment with propylene), the following chromatogram was observed: a peak emerging with $T_m = 100°C$ and a group of peaks in the temperature interval of 200–285°C (Fig. 3). The products emerging up to 160°C were trapped and analyzed. These were found to consist of propane and a small amount of propylene (Fig. 4). In all probability the propylene molecules chemisorbed on the catalyst become hydrogenated when the catalyst temperature was increased. This experiment could be taken as an indication of the lowest initial temperature at which the hydrogenation of propylene over NiO occurs.

From the peak area in the thermodesorption chromatogram for ethylene (the first peak in Fig. 2a) the amount of desorbed ethylene was determined as 3.15×10^{-3} cm^3 by the absolute calibration method. This volume corresponded to 7.9×10^{16} molecules of ethylene (converting to the volume under standard conditions and multiplying by Loschmidt's number of 2.68×10^{19} molecules in 1 ml). According to literature data (*8*) the surface occupied by one adsorbed ethylene molecule is equal to 43 Å² so that the total area covered with ethylene molecules is 3.4×10^{18} Å² (3.40×10^{-2} m²). With the total catalyst surface of 30.2 m² this amounts to 0.11% of the total catalyst surface. This is the area on which the reversible chemisorption of ethylene takes place. The surface coverages calculated from the thermodesorption chromatograms obtained in the various experiments amounted to 0.08–0.15% of the total surface of NiO–catalyst.

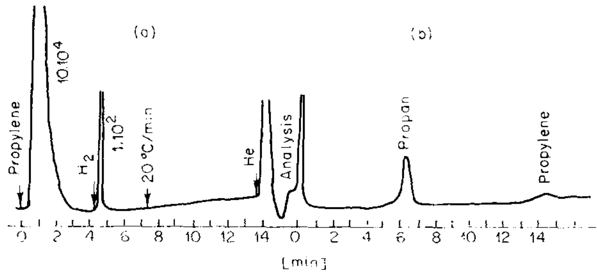

FIG. 4. (a) Thermodesorption chromatogram (Expt. as in Fig. 3) with refrigeration of products appearing up to 160°C; (b) analytical chromatogram of these products.

REFERENCES

1. KUBOKAWA, Y., ADACHI, T., TOMINO, T., AND OTZAWA, T., *Int. Congr. Catal., 4th, Moscow, 1968,* paper 39.
2. ADAMS, C. R., AND JENNINGS, T. J., *J. Catal.* **2,** 63 (1963).
3. MARGOLIS, L. Y., *Int. Congr. Catal., 4th, Moscow, 1968,* paper 19.
4. KRILOV, O. V., *Probl. Kinet. Katal.* **12,** (1968).
5. ENIKEEV, E. K., MARGOLIS, L. Y., AND ROGINSKII, S. Z., *Dokl. Akad. Nauk USSR,* **124,** 606 (1959).
6. ENIKEEV, E. K., ISAEV, O. V., AND MARGOLIS, L. Y., *Kinet. Katal.* **1,** 431 (1960).
7. MORO-OKA, Y., AND OZAKI, A., *J. Amer. Chem. Soc.* **89,** 5124 (1967); *Int. Congr. Catal. 4th, Moscow, 1968,* paper 17.
8. AMENOMIYA, Y., AND CVETANOVIC, R. J., *J. Phys. Chem.* **67,** 144 (1963).
9. AMENOMIYA, Y., AND CVETANOVIC, R. J., *J. Phys. Chem.* **67,** 2046 (1963).
10. EHRLICH, G., AND HICKMOTT, T. W., *Nature (London)* **177,** 1045 (1956).
11. HICKMOTT, T. W., AND EHRLICH, G., *J. Chem. Phys.* **24,** 1263 (1956).
12. YAKERSON, V. I., ROZANOV, V. V., AND RUBINSHTEIN, *Surface Sci.* **12,** 221 (1968).
13. REDHEAD, P. A., *Trans. Faraday Soc.* **57,** 641 (1961).