Determination of the Chemical Properties of an Oxide Catalyst in a Closed System

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The bulk chemical properties of an impregnated chromia-alumina catalyst with respect to several gases, CO, CO_2, C_3H_6, were determined as a function of the degree of oxidation of the surface of the catalyst. The importance of the results lies in the demonstration that a simple method described herein can be used to obtain significant data on catalytic surfaces. Briefly, the prior adsorption of oxygen by the catalyst tended to promote the adsorption of carbon monoxide and to prohibit the adsorption of carbon dioxide. Far more carbon monoxide was adsorbed by the highly oxidized surface than could be accounted for on the basis of adsorbed carbon dioxide. The quantity of propylene adsorbed also increased with an increase in the oxidation of the surface. The results are explained on the basis of two types of adsorbed oxygen atoms.

The importance of catalysts in the chemical industries initiated this investigation, one of the objectives of which was to determine some chemical properties of the surface of an oxide catalyst. Use of a closed system permitted separate examinations of various portions of the catalyst surface. The method of approach described herein is not proposed as a substitute for the flow-type experiments described by Hougen and Watson (*6*). It is instead suggested as an independent approach to be used in conjunction with the usual flow-type experiments to give a better understanding of the manner in which a catalyst participates in a given chemical reaction.

Past investigations of catalysts in closed systems may be divided into two classes, those involving physical adsorption and those involving chemical adsorption. Except in the measurement of the surface area of the catalyst, the adsorptions involved in this investigation were of the chemical type. Most of the previous experimentation concerning this type of adsorption has been pointed toward showing either the heterogeneity or homogeneity of catalyst surfaces. H. S. Taylor and coworkers (*8*, *9*, *10*) have interpreted the results of their investigations, which involved the adsorption of hydrogen by technical catalysts, as showing the heterogeneity of technical catalyst surfaces. On the other hand, Roberts (*7*), Beeck (*2*), and Eucken (*4*) have investigated pure metal catalysts, usually in the form of films, and found that all adsorption sites on them behaved in essentially the same manner, which led them to conclude that the surfaces possessed a high degree of homogeneity.

The oxidized surface of the catalyst investigated here could be described in terms of two basic groups of sites, and within each group these sites appeared to exhibit homogeneous behavior.

Most of the catalysts used commercially contain several components. In view of this a rather complex catalyst was selected for the investigation in order to determine whether or not the bulk chemical properties of its surface could be explained in a relatively simple manner, as described above. The catalyst selected contained oxides of chromium, iron, and potassium supported on alumina. The percentages by weight of Cr_2O_3, Fe_2O_3, K_2O, and Al_2O_3 were 20, 3, 2,

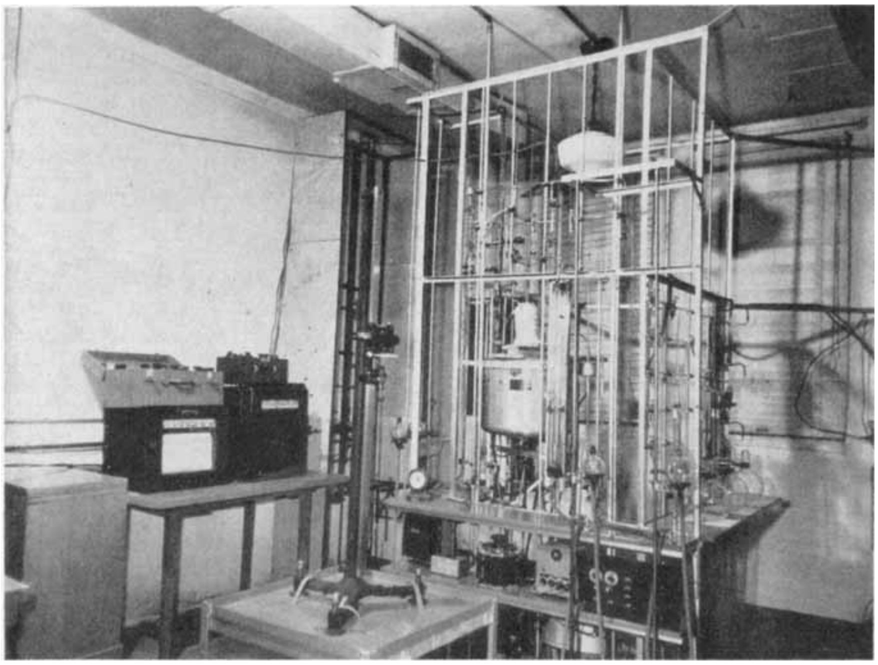

Fig. 1A. Adsorption apparatus.

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and 75 respectively. The chemical properties of the surface of this catalyst at various degrees of oxidation with respect to carbon dioxide, carbon monoxide, propylene, and oxygen (following the prior adsorption of propylene) were determined.

The importance of the results lies in the demonstration that a simple method can be used to obtain significant data, rather than in the detailed properties of the particular surface used.

DESCRIPTION OF APPARATUS

An adsorption apparatus suitable for measuring the quantities of a gas adsorbed, desorbed, and reacted in the presence of an oxide catalyst was constructed. The arrangement of the apparatus, shown in Figure 1, is in many respects similar to the one proposed by Brunauer, Emmett, and Teller (*3*) for surface-area determinations. The auxiliary equipment consisted of the following: (1) a constant-temperature water bath from which water was circulated through the burette jacket, (2) several appropriate constant-temperature baths used to maintain the catalyst bulb at the desired temperatures, (3) a vapor-pressure thermometer (M_2 was a part of this thermometer) constructed so that it might also be used as a Toepler pump, (4) a pressure controller which maintained the system pressure constant by adjusting the mercury level in the burette, (5) a mercury-condensation pump preceded by a mechanical vacuum pump, and (6) a cathetometer for reading manometers M_1 and M_2. A detailed description of the apparatus is given in reference *5*.

EXPERIMENTAL PROCEDURE

The manipulation of the various stopcocks necessary to effect the adsorption and desorption experiments has been described in reference *5*. It is in many respects similar to that used in the Brunauer, Emmett, and Teller surface-area determinations. The behavior of the catalyst, at various degrees of oxidation, in the presence of each of the gases mentioned previously was determined by adsorption and desorption experiments. When any of the gases reacted with previously adsorbed substances on the surface of the catalyst, the necessary gas samples were analyzed by use of a mass spectrometer. These experiments were performed with the catalyst at a temperature of 550°F. Adsorption experiments were carried out at a constant pressure of 73.2 cm. Hg. abs.

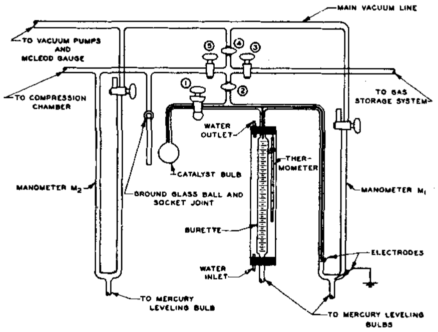

Fig. 1B. Adsorption apparatus.

The catalyst was stabilized by alternately oxidizing and reducing it until the change of its chemical adsorption properties with age (time) was negligible. A surface area of 72.6 sq. m./g. was obtained through the method proposed by Brunauer, Emmett, and Teller (*3*) for a fresh sample of the catalyst and an area of 64.5 sq. m./g. was obtained for the stabilized catalyst. After each experiment the catalyst was thoroughly cleaned by alternately oxidizing and reducing it ten times at 980°F. This process was carried out over a period of about 3 days. After the final reduction, the catalyst was evacuated for approximately 12 hr. for the purpose of removing any hydrogen which might have been adsorbed during the final reduction. Close agreement between oxygen adsorption and the hydrogen uptake during reduction indicated that little or no oxidizable hydrogen was retained on the reduced surface after evacuation. Similar behavior has been observed for chromia supported on alumina (*11*), but not for pure chromic oxide (*12*). In spite of the severity of the cleaning process employed, it was difficult to return the catalyst to the same degree of cleanliness each time. The experimental procedure was repeated precisely, but the cleanliness of the surface of the catalyst could not be.

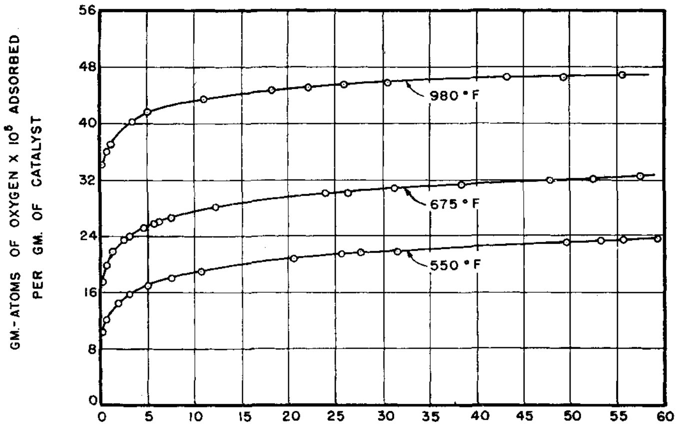

Fig. 2. Adsorption of oxygen.

After the catalyst had been reduced and cleaned, the oxygen was adsorbed on it, the amount being dependent upon both time and temperature. It could be removed quantitatively with hydrogen. Throughout this paper the quantities of gases adsorbed are, for convenience, referred to as 10^5 times the actual values. The results of these experiments are shown in Figure 2. For oxygen adsorptions of about 16.0 g.-atoms/g. of catalyst, an adsorption temperature of 550°F. was employed. Temperatures of 675° and 980°F. were used when it was desired to adsorb quantities of oxygen in the neighborhood of 24 and 45 g.-atoms, respectively. The adsorption of oxygen was essentially irreversible. Each adsorption experiment was followed by a desorption experiment for the purpose of measuring any small quantity of oxygen which could be desorbed. After the oxygen surrounding the catalyst had been removed, the gas to be studied was admitted to the catalyst and the quantity of the gas adsorbed (or the change in volume at constant pressure) was measured. The residual gas surrounding the catalyst and products which desorbed readily from the surface of the catalyst were withdrawn, measured, placed in a sample container, and analyzed by use of a mass spectrometer. The information obtained from the experiments was used to make an over-all material balance, which established quantitatively the final state of the catalyst with respect to adsorbed substances. The results of the experimental investigations follow. The original data are given in reference *5*.

EXPERIMENTAL RESULTS

Carbon Dioxide Experiments

In these experiments the action between carbon dioxide and the catalyst at different degrees of oxidation was determined, and the results of these experiments are shown in Figure 3. The upper curve represents the amount of carbon dioxide adsorbed on the surface of the catalyst, and the lower curve shows the amount remaining after desorption. About 75% of the carbon dioxide was adsorbed during the first 30 sec. of each experiment. The experiments were carried out for several hours, and at the end of that time the rate of adsorption was very nearly zero.

Examination of the results showed that as the amount of oxygen initially adsorbed on the hydrogen-reduced catalyst was increased, the adsorption of carbon dioxide by the catalyst decreased.

Carbon Monoxide Experiments

A set of experiments was devised for the purpose of ascertaining the behavior of carbon monoxide and the catalyst at various degrees of oxidation. The first step in these experiments consisted of the adsorption of the desired quantity of oxygen on the hydrogen-reduced catalyst. Then the catalyst, at the resulting state of oxidation, was treated with carbon monoxide for a period of 3 min., after which all adsorption and reaction appeared to have been completed. The gas in the dead space (the space bounded by the catalyst bulb and stopcock 1) was then withdrawn, measured, and analyzed. For the lower initial adsorptions of oxygen by the catalyst, a single treatment of the catalyst with carbon monoxide was sufficient. However, in the investigation of the catalyst at its most highly oxidized state, it was necessary to treat it several times with carbon monoxide. The first few times it was treated, the catalyst bulb became filled with carbon dioxide and limited the extent of the adsorption and reaction processes. The results of these experiments are shown in Figure 4. The deviation of the two points from the two curves (at 18.8 g.-atoms of oxygen initially adsorbed) is attributed to the limiting effect of the size of the bulb for the single treatment of carbon monoxide employed in that particular experiment.

In Figure 4 the carbon monoxide which remained adsorbed on the catalyst, in the form of either carbon monoxide or carbon dioxide, was calculated as carbon monoxide and is referred to as *carbon monoxide adsorbed.* Upon examination of the experimental results, it is seen that both carbon monoxide adsorption and the reaction of carbon monoxide with adsorbed oxygen to produce carbon dioxide increased as the previously adsorbed oxygen was increased. In the experiment in which the catalyst contained initially 45.2 g.-atoms of adsorbed oxygen, upon treatment of this catalyst with carbon monoxide, 13.6 g.-atoms reacted to produce carbon dioxide which was evolved to the gas phase; associated with the remaining 31.6 g.-atoms of oxygen was 28.0 g.-atoms of carbon monoxide. On the basis of the ratio obtained, 28/31, one would be led to conclude that carbon monoxide was adsorbed on the catalyst in the form of carbon dioxide. However, from the results of the carbon dioxide experiments, one would not have expected more than 10 g.-moles of carbon dioxide to have been adsorbed. From both sets of experiments, on carbon monoxide and dioxide, it appears that some of the carbon monoxide was adsorbed in some form other than as carbon dioxide.

Propylene Experiments

These experiments consisted of treating the catalyst, at various degrees of oxidation, with propylene. When propylene had been in contact with the catalyst for 8 min., the adsorption appeared to have been completed. Then the gas surrounding the catalyst was withdrawn, measured, and analyzed. The results of these experiments are shown in Figure 5. Upon examination of these results it is seen that the quantity of carbon adsorbed

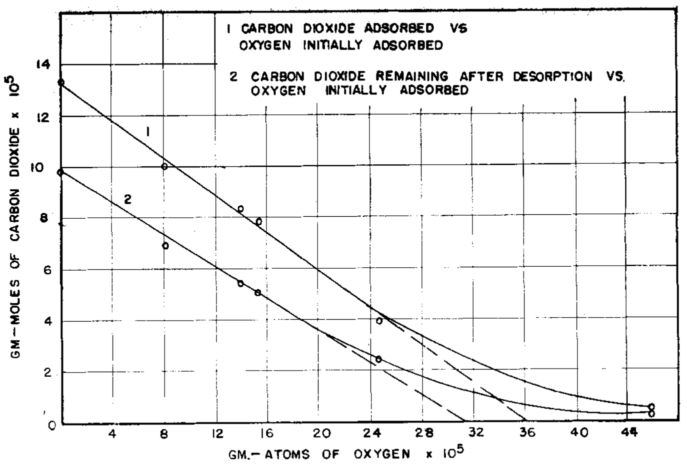

Fig. 3. Adsorption of carbon dioxide.

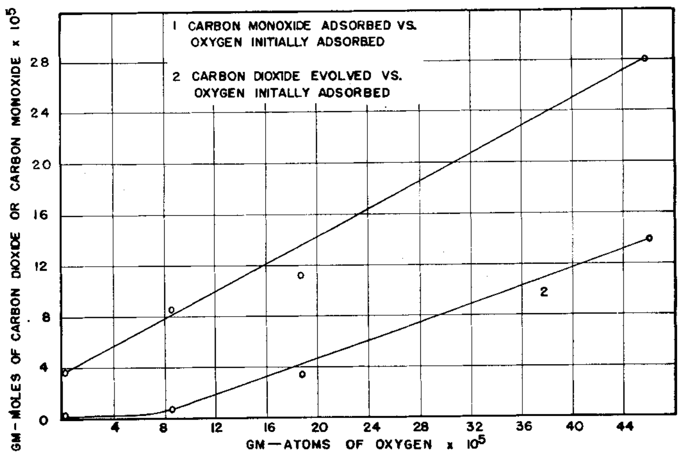

Fig. 4. Adsorption and reaction of carbon monoxide.

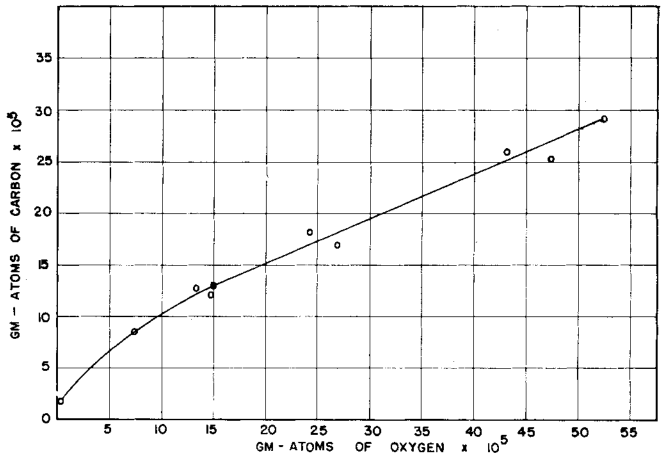

Fig. 5. Adsorption of propylene.

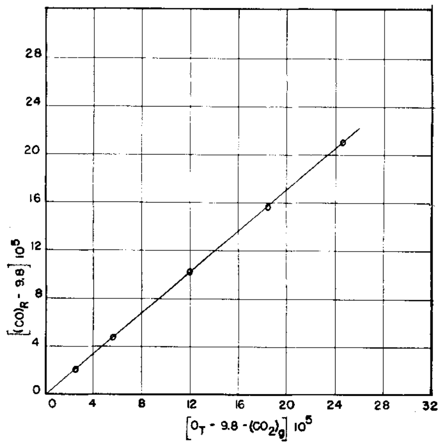

Fig. 6. Test of carbon monoxide correlation.

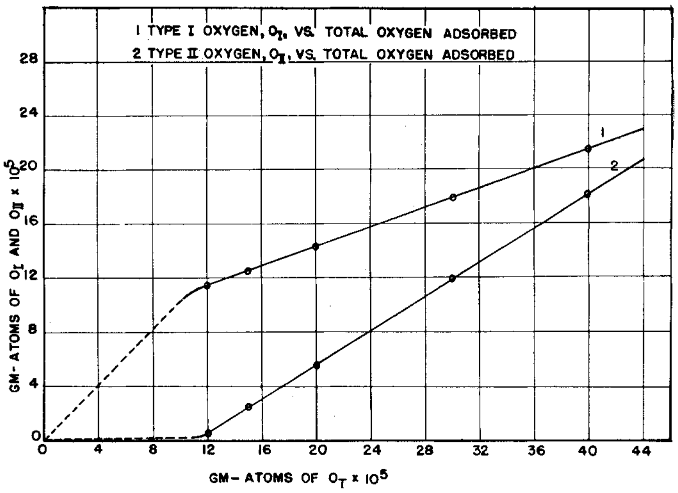

Fig. 7. Oxygen distribution.

increased as the amount of oxygen initially adsorbed was increased. In addition to the retention of carbon, the catalyst also adsorbed hydrogen. As the amount of oxygen initially adsorbed was varied from 7.69 to 45.8 g.-atoms, the hydrogen-carbon ratio varied from 1.89 to 1.93. The gas withdrawn from the vicinity of the catalyst contained a corresponding amount of propane, thereby having a hydrogen-carbon ratio greater than 2.0. The reduced catalyst did not promote hydrogen transfer.

Oxidation products such as carbon monoxide and dioxide were not detected in the gas sample. Had an appreciable quantity of carbon dioxide been formed, the results of the carbon dioxide experiments indicate that some of this gas would have been desorbed in the process of the removal of the gas sample. In view of the results of the experiments with carbon monoxide and dioxide and with propylene, it appears that the carbon and hydrogen were adsorbed in the form of a carbon-hydrogen molecule rather than as carbon monoxide and dioxide.

Oxidation of the Catalyst Containing Adsorbed Propylene

After the catalyst had been treated with propylene as described above, oxygen was admitted to it. The principal fact established was that essentially all the adsorbed propylene reacted with the oxygen, giving carbon dioxide, water, and traces of carbon monoxide. Since the gas samples were not analyzed for water, the numerical results are not stated; however, the qualitative result is worthy of mention, in view of the failure of propylene to react with adsorbed oxygen to yield oxidation products.

DISCUSSION AND INTERPRETATION

The results of the carbon monoxide experiments indicate that the oxidized catalyst contained adsorbed oxygen atoms of different character; one type reacted with carbon monoxide to give carbon dioxide, and the other type adsorbed carbon monoxide. These are referred to as types I and II, respectively. In any correlation of the results of the carbon monoxide experiments it apparently would be necessary to use the concept of two types of adsorbed oxygen atoms.

There are perhaps several ways in which the results of the carbon monoxide, carbon dioxide, and propylene experiments could be correlated. One method, believed adequate and representative of the properties of the catalyst, is shown here. Although empirical, it is remarkably simple and straightforward. Other methods are of course not excluded.

Correlation of the Carbon Monoxide Results

Interpretation of the results on carbon monoxide entails the concept of two types of adsorbed oxygen atoms, and the carbon dioxide results are also used, as some of the carbon monoxide which was retained could have been adsorbed in the form of carbon dioxide.

To type II adsorbed oxygen atoms is attributed the adsorption of carbon monoxide as such. Thus,

$$(\mathrm{CO})_a = \alpha \mathrm{O}_{\mathrm{II}} \qquad (1)$$

Of the total carbon monoxide remaining on the catalyst, not more than 9.8 g.-moles could have remained in the form of carbon dioxide. (See Figure 3.) If it is assumed that these sites were always available for the adsorption of carbon dioxide, then the expression for the total amount of carbon monoxide remaining adsorbed on the catalyst in the form of either carbon monoxide or dioxide is

$$(\mathrm{CO})_R = 9.8 + \alpha \mathrm{O}_{\mathrm{II}} \qquad (2)$$

This equation is applicable to those experiments where the quantity of oxygen initially adsorbed was sufficient for the production of 9.8 g.-moles of carbon dioxide.

All the carbon dioxide formation is attributed to the adsorbed oxygen of type I. Part of this carbon dioxide, 9.8 g.-moles, was retained by the catalyst and the remainder was evolved to the gas phase, because of the lack of adsorption sites. Thus,

$$\mathrm{O}_{\mathrm{I}} = (\mathrm{CO}_2)_g + 9.8 \qquad (3)$$

Since only two types of adsorbed oxygen atoms were proposed, the total quantity of oxygen adsorbed prior to a carbon monoxide experiment is given by

$$\mathrm{O}_T = \mathrm{O}_{\mathrm{I}} + \mathrm{O}_{\mathrm{II}} \qquad (4)$$

Elimination of O_{I} and O_{II} from these equations results in

$$(\mathrm{CO})_R - 9.8 = \alpha[\mathrm{O}_T - 9.8 - (\mathrm{CO}_2)_g] \qquad (5)$$

Values of $(\mathrm{CO})_R$ and $(\mathrm{CO}_2)_g$ corresponding to given values of O_T were read from the smooth curves shown in Figure 4. A plot of Equation (5) is shown in Figure 6. Support of the correlation of the carbon monoxide results is given by the linearity and zero intercept of the line shown in Figure 6. The slope α of the line was found to be 0.847.

The oxygen distribution, O_{I} and O_{II} as functions of O_T (for O_T greater than 9.8), was obtained by use of Equations (3) and (4). Graphical representation of it is given in Figure 7. For oxygen adsorption less than 9.8, O_{I} was taken approximately equal to O_T, indicated by the broken lines. This distribution was used to correlate the results of the propylene experiments, as shown below.

Correlation of the Propylene Results

If the adsorption of propylene could be attributed to either one of the two types of oxygen, then one of the two

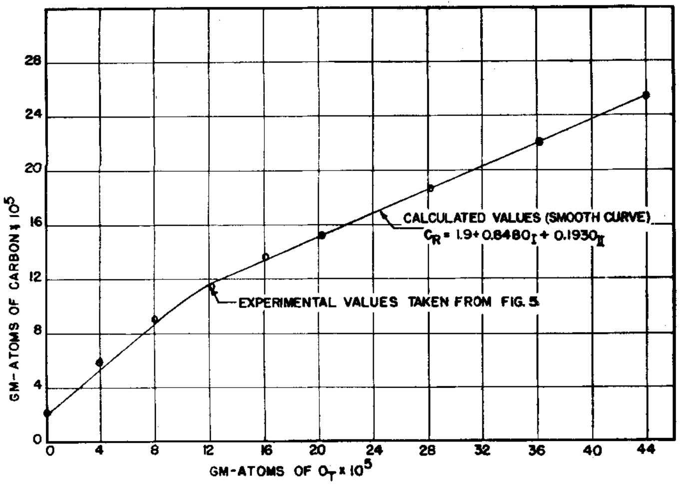

Fig. 8. Correlation of results of propylene experiments.

constants, β and γ, in the following equation would be equal to zero.

$$C_R = 1.9 + \beta O_I + \gamma O_{II} \qquad (6)$$

The constant, 1.9, represents the quantity of carbon adsorbed on the reduced catalyst. The best correlation of the propylene results was obtained by taking $\beta = 0.848$ and $\gamma = 0.193$. By means of these values and the oxygen distribution, a comparison of the calculated and experimental values of the carbon adsorbed is shown in Figure 8. The agreement of these indicates that both types of oxygen were involved in the adsorption of propylene.

Correlation of the Carbon Dioxide Results

Of the total carbon dioxide adsorbed, part of it was strongly held but the remainder was weakly held and could be desorbed readily. Essentially all the carbon dioxide sites covered by the prior adsorption of oxygen can be accounted for on the basis of the extrapolated straight lines shown in Figure 3. The equations are as follows:

$$(CO_2)_T = 13.62 - 0.361\, O_T \qquad (7)$$

$$(CO_2)_S = 9.8 - 0.331\, O_T \qquad (8)$$

Subtracting Equation (8) from (7) gives the expression for the weakly held carbon dioxide.

$$(CO_2)_W = 3.4 - 0.05\, O_T \qquad (9)$$

These relationships indicate that the carbon dioxide sites were covered indiscriminately by oxygen of types I and II.

It is of interest to compare the coefficients in Equations (1) and (6) with the mole ratio of chromium to iron in the catalyst sample. The latter contained 0.875 atom of chromium/0.125 atom of iron. The experimental coefficients of 0.847, 0.848, and 0.193 are of the same order of magnitude as the chromium-iron ratio. Although this correspondence does not certify the following relationship between the behavior of the catalyst and its composition, it does suggest that about 87% of the O_I was adsorbed on chromium and the remainder of the O_I was adsorbed on iron; whereas, 87% of the O_{II} was adsorbed on iron, while the remainder of the O_{II} was adsorbed on chromium. Furthermore, carbon monoxide was adsorbed by oxygen of type II on iron, and propylene was retained by oxygen of type I on chromium as well as by oxygen of type II on chromium.

It should be pointed out that the determination of the relationship between catalyst behavior and catalyst composition was not an object of the original investigation. The relationship suggested is an interesting consequence of the correlations.

CONCLUSIONS

The chemical properties, as illustrated by use of the surface of an oxide catalyst, are useful in interpreting the catalytic behavior of surfaces. It was possible to explain the behavior of the surface of the catalyst used on the basis of two types of adsorbed oxygen atoms. In view of the information obtained for this technical oxide catalyst, it appears that this method of approach should prove useful in the study of catalysts.

ACKNOWLEDGMENT

This work was supported through the cooperation of the Texas Engineering Experiment Station, The Gulf Oil Company, and the Magnolia Petroleum Company.

NOTATION

C_R = atoms of carbon retained by the catalyst after any given propylene experiment
$(CO)_a$ = moles of carbon monoxide adsorbed on the catalyst in some form other than that of carbon dioxide
$(CO)_R$ = total moles of carbon monoxide adsorbed (in the form of either carbon monoxide or dioxide) by the catalyst during any given carbon monoxide experiment
$(CO_2)_g$ = moles of carbon dioxide formed and evolved to the gas phase during any given carbon monoxide experiment
$(CO_2)_S$ = moles of carbon dioxide strongly adsorbed in any given carbon dioxide experiment
$(CO_2)_T$ = total moles of carbon dioxide adsorbed in any given carbon dioxide experiment
$(CO_2)_W$ = moles of carbon dioxide weakly adsorbed in any given carbon dioxide experiment
O_I = moles of adsorbed oxygen of Type I; this type reacted with carbon monoxide to produce carbon dioxide
O_{II} = moles of adsorbed oxygen of type II; this type was responsible for the adsorption of carbon monoxide in some form other than that of carbon dioxide
O_T = total moles of adsorbed oxygen; it is equal to the sum of types I and II
α = proportionality constant defined by Equation (1)
β, γ = proportionality constants defined by Equation (6)

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