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# Energetic Nature of Catalyst Surfaces

## I. Supported Cobalt on Rutile

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A system for investigating the energetic nature of catalyst surfaces has been developed from thermal desorption experiments. By applying an incremental isothermal heating program to the studies, the desorption kinetics have been analyzed to yield the variation in activation energy of desorption with coverage. The technique has been used to study a supported cobalt catalyst and, by following the desorption of hydrogen, the nature of the surface has been studied during reduction, and after a series of hydrogenolysis reactions had been conducted on the surface.

## INTRODUCTION

Almost all surfaces can be defined by a distribution of adsorption sites with varying adsorption energy. This is because of the presence of different crystal faces, edges, imperfections, impurity centers, as well as the degree of crystallographic order of the atoms at the surface of the solid. The degree of order at the surface, as well as in the bulk, is of primary concern when metal catalysts are prepared by reduction of the metal oxide by hydrogen. Many techniques have been used to study surfaces. These include field electron and field emission microscopy, low energy electron diffraction, chemisorption and flash desorption.

Flash desorption techniques have been used for some time to study catalyst surfaces (*1, 2*). More recently the same technique has been used to study the desorption of hydrogen from metal catalysts (*3–5*), and distinguish different types of bonding from the different energies of desorption. A series of runs conducted at different heating rates are required to obtain the activation energy profile from flash desorption experiments.

An alternative to this approach of using a linear or exponential heating program has been the use of an incremental isothermal heating program to study the energetic nature of the surface oxide on carbons and graphite (*6–8*). With such a program only one desorption experiment is required. This was necessary in the study of carbon and graphite as removal of the oxide as carbon monoxide and carbon dioxide removed carbon atoms from the surface, which was therefore continually changing.

Basically the desorption process was monitored as the sample is held at a constant temperature for predetermined times. The temperature was then abruptly raised by a given increment and the desorption process again followed. This procedure was repeated, the time and temperature intervals being chosen to suit the specific system being measured. The activation energy of desorption could be determined by analysis of the desorption kinetics in each temperature interval. By plotting the rate of desorption with respect to the amount desorbed at adjacent temperature intervals, and by a small extrapolation, the rates of desorption at two temperatures corresponding to the same amount desorbed can be determined and by using the relationship,

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$$\log_{10}\left[\frac{\text{desorption rate at } T_1}{\text{desorption rate at } T_2}\right]_\theta = \frac{E_\theta}{2.3R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right],$$

the Arrhenius activation energy, $E$, at coverage $\theta$ (or amount desorbed) could be calculated. Repeating the calculation at each temperature "step" allowed the variation in $E$ as a function of coverage to be measured. To be strictly correct, in the absence of a defined reaction, the calculated values of $E$ are actually temperature coefficients.

## EXPERIMENTAL METHODS

The apparatus shown in Fig. 1 was essentially the same as that used in previous studies (*6–8*), except that a high speed diffusion pump was positioned between the sample and the reservoir volume. This diffusion pump was used to transfer the desorbed gas into the reservoir. This maintained a high vacuum over the sample during desorption, and so eliminated any readsorption of the desorbed gas back onto the sample. It was important that a diffusion pump with a high critical backing pressure be chosen for this purpose, as the pressure build up in the reservoir must not exceed this critical pressure or the pump would stall. The general procedures employed were basically the same as those used previously (*6*, *7*). The partial pressure of each gaseous component in the reservoir volume has been shown to be directly proportional to the ion current measured on the mass spectrometer (*8*). By using a mass spectrometer instead of a total pressure gauge the composition of the desorbed gas could be analyzed and, in the case of hydrogen adsorption–desorption used, to confirm that only hydrogen is in fact desorbed.

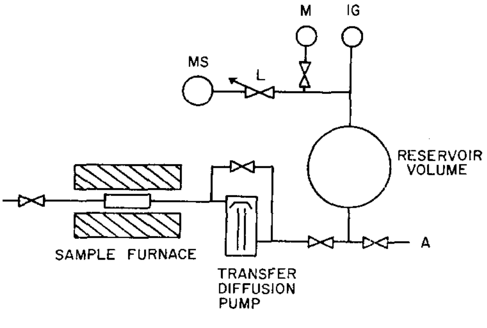

FIG. 1. Thermal desorption apparatus: (A) vacuum and gas supply; (MS) mass spectrometer; (L) leak valve; (M) McLeod gauge; (IG) ionization gauge.

A supported cobalt catalyst has been used in these studies, and was prepared by impregnating a nonporous rutile support obtained from British Titan Products (33 $m^2\ g^{-1}$ surface area) with cobalt nitrate. The catalyst was dried at 120°C and then pressed into discs. X-Ray diffraction studies at this stage showed weak reflections pertaining to $Co_3O_4$. Analysis of the catalyst showed it to contain 4% cobalt wt/wt.

The catalyst was reduced *in situ* at 330°C with a flow of 50 ml/min of purified hydrogen. Before a desorption run was initiated the catalyst was cooled from the reduction temperature down to room temperature under an atmosphere of hydrogen. The sample was then evacuated for 2 min before the desorption kinetics were monitored.

Hydrogen adsorption was measured on a conventional volumetric adsorption system similar to that described by Feath (*9*). The catalyst was again reduced *in situ* before recording the extent of hydrogen adsorption.

## RESULTS AND DISCUSSION

Figure 2 shows typical hydrogen desorption curves from the catalyst at each temperature as the sample was heated by the

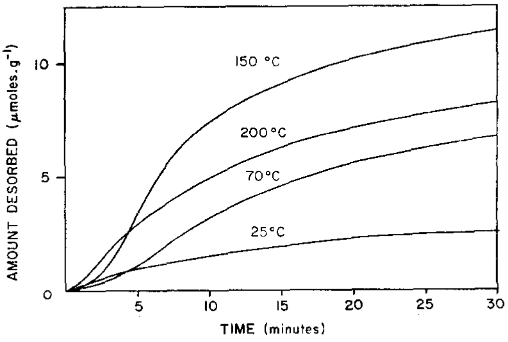

FIG. 2. Typical desorption curves.

incremental isothermal temperature program. The catalyst had been reduced for 3 days before taking these measurements. Higher desorption temperatures were not used at this stage as it was feared that the use of higher temperatures may cause a reduction of the metal surface area by sintering.

The desorption curves have been found to obey the Elovich equation

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

where $q$ is the amount desorbed at time $t$ and $a$ and $\alpha$ are constants. This equation seems to have a general applicability to chemisorption data (*10*), and is more commonly used in its integrated form, viz.,

$$q = \frac{1}{\alpha}[\log(t + t_0) - \log(t_0)],$$

where $t_0 = 1/\alpha a$.

In this form it is possible to plot the quantity of gas desorbed against log $(t + t_0)$, the value of $t_0$ being chosen to linearize such plots. This is illustrated in Fig. 3 for the desorption curves shown in Fig. 2.

Computer analysis of these plots, to find the value of $t_0$ that will linearize them, is shown in Table 1 for the above data. From this table it is apparent that values of $t_0$ of the order of a few minutes simply relate to the inability to determine with any precision the time at which the sample reaches its required temperature at each temperature increment. The much larger

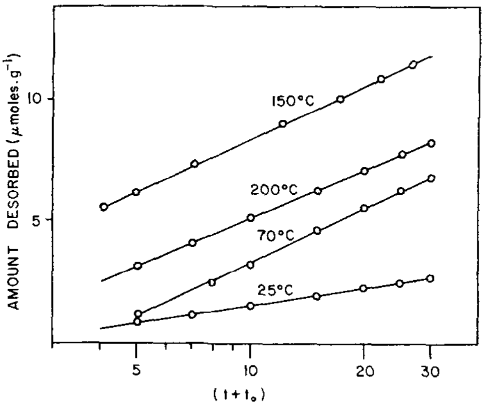

FIG. 3. Elovich plots of the curves shown in Fig. 2.

TABLE 1
ELOVICH CONSTANT $t_0$

| Desorption temp (°C) | $t_0$ |
|---|---|
| 70 | 2.3 |
| 150 | −3.4 |
| 200 | −0.4 |
| 250 | 1.6 |
| 300 | 1.2 |
| 340 | 9.1 |

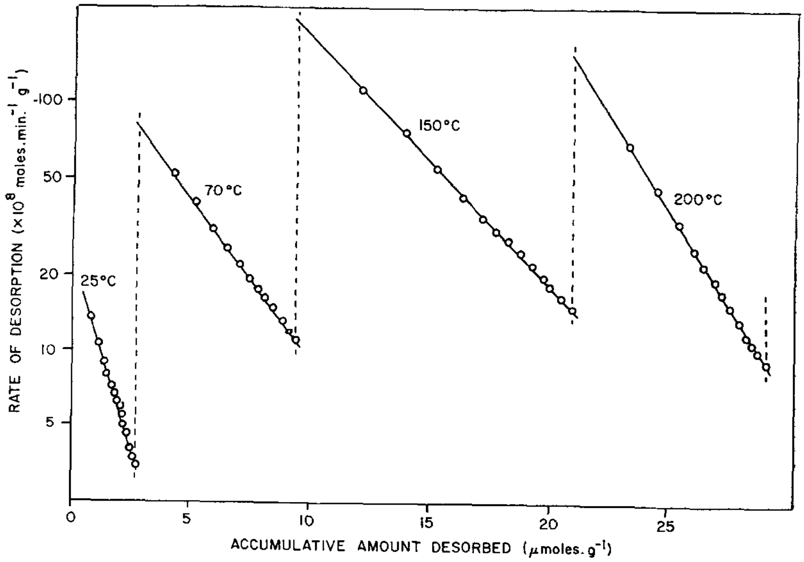

FIG. 4. Rates of desorption at each temperature plotted against the amount of hydrogen desorbed.

value found at 340°C is significant, and is discussed below.

Rate data obtained from these desorption curves is shown in Fig. 4 plotted as log (rate of desorption) versus accumulative amount desorbed. This is obtained by fitting the desorption curves to an *n*th degree polynomial which can be easily differentiated to obtain rate data (*7*). Analysis of Fig. 4 by the method described allows the computation of *E* at each temperature increment. The variation in *E* with amount desorbed for the catalyst reduced for 3 days is shown in Fig. 5.

Reduction of the catalyst for a further 3 days has been found to significantly affect the shape of the curve as shown in Fig. 6. It can be seen that the higher energy sites, after an extra 3 days reduction, have been reduced in energy and are beginning to form a plateau at about 20 kcal/mole.

After the catalyst had been used to measure the rates of ethane, propane and butane hydrogenolysis over the catalyst, further desorption kinetics were measured. These experiments showed the surface to be even more homogeneous as can be seen from Fig. 7.

Comparison of Figs. 5–7 is very instructive and illustrates a significant ordering of the cobalt surface. After 3 days reduction the surface is still heterogeneous (cf. Fig. 5), but with continued reduction the surface becomes more homogeneous towards the desorption of hydrogen with an energy of 21 kcal/mole.

Hydrogen adsorption measurements have

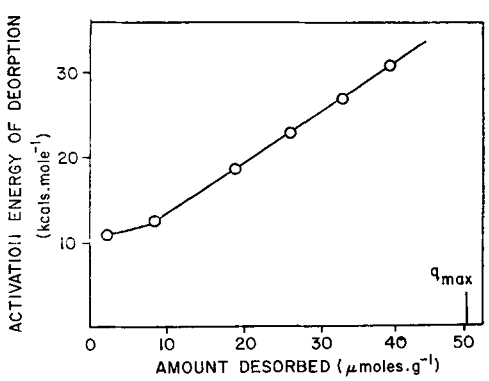

FIG. 5. Variation of the activation energy of desorption with amount desorbed after 3 days reduction. $q_{max}$ corresponds to the total amount desorbed on degassing to 340°C.

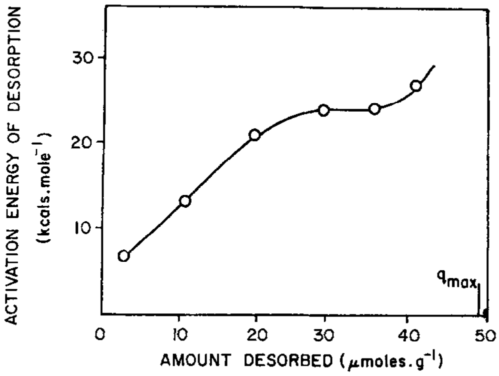

FIG. 6. Variation of the activation energy of desorption with amount desorbed after 6 days reduction. $q_{max}$ again corresponds to the total amount desorbed on degassing to 340°C.

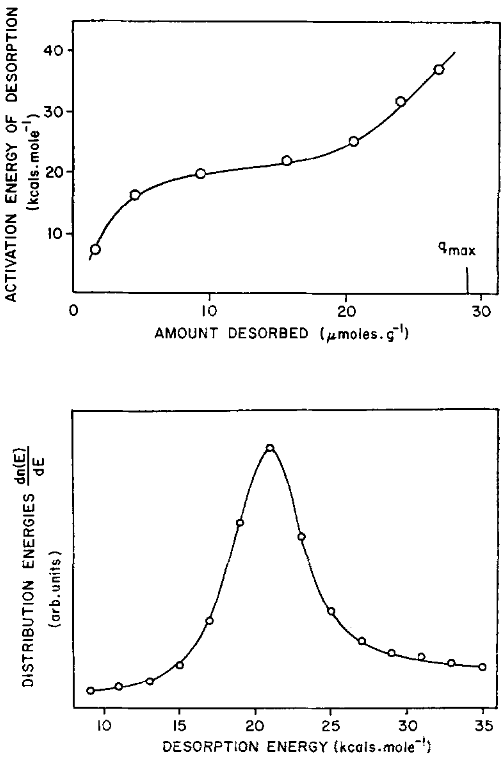

FIG. 7. Variation after the catalyst had been used to measure rates of hydrogenolysis and the distribution of energies present.

TABLE 2
TEMPERATURE VARIATION STUDIES OF HYDROGEN ADSORPTION

| Adsorption temp (°C) | Vol adsorbed (ml $H_2$ (STP)/g catalyst | Hydrogen pressure (cm Hg) |
|---|---|---|
| 300 | 0.475 | 44.66 |
| 200 | 0.480 | 44.29 |
| 100 | 0.494 | 43.69 |
| 23 | 0.498 | 43.04 |
| −78 | 0.542 | 41.33 |
| −195 | 3.469 | 36.02 |
| −78 | 0.542 | 41.33 |
| 23 | 0.509 | 42.99 |
| 100 | 0.510 | 43.62 |
| 200 | 0.504 | 44.18 |
| 300 | 0.466 | 44.70 |

also been recorded on a similar sample of catalyst reduced for 3 wk prior to use. It was found that the adsorption was activated. Negligible adsorption was found when the catalyst was degassed at 300°C, and then cooled to 25°C before admission of the hydrogen, although significant hydrogen was adsorbed at 300°C. Table 2 shows the variation of amount adsorbed using the temperature variation method of Taylor and Liang (*11*). Twenty-four hours were allowed between each measurement to ensure equilibrium had been reached. The quantity of hydrogen adsorbed as the temperature is dropped to 23°C agrees closely to that desorbed during desorption experiments when the sample is heated from room temperature to 300°C, the temperature used to degass catalyst during adsorption measurements. It is also apparent from the table that the amount of hydrogen adsorbed increases significantly below −78°C at which temperatures physical adsorption becomes prominent.

Total hydrogen desorption can only be accomplished by heating the catalyst to temperatures where sintering occurs. This can therefore only be done when the catalyst is no longer required. The incremental and accumulative amounts of hydrogen desorbed on heating the catalyst in 50°C intervals to 550°C are shown in Fig. 8. The figure clearly shows two peaks in the incremental desorption curve at 200 and 500°C. Analysis of the desorption kinetics yields the variation in *E* and distribution curve shown in Fig. 9.

The desorption peaks can now be related to the two plateau regions in Fig. 9 with desorption energies of 21 and 33 kcal/mole.

Other investigators have also reported two or more desorption peaks (*2*, *4*, *5*) for the desorption of hydrogen from metal catalysts although several reasons have been advanced for this phenomena. Contour and Pannetier (*4*) observed two desorption peaks on a γ-alumina supported iridium catalyst while the unsupported iridium produced only one peak. They interpreted their results in terms of a metal–support interaction, which also produced a more loosely bound hydrogen atom. Popova, Babenkova, and Sokol'skii (*5*) also found two peaks with some nickel supported catalysts, although with certain supports they only observed one peak.

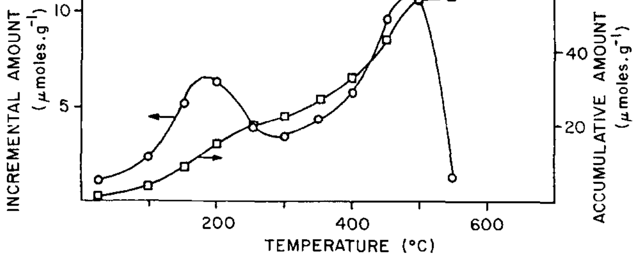

FIG. 8. Incremental and accumulative amounts desorbed on heating the catalyst in 50°C intervals to 550°C.

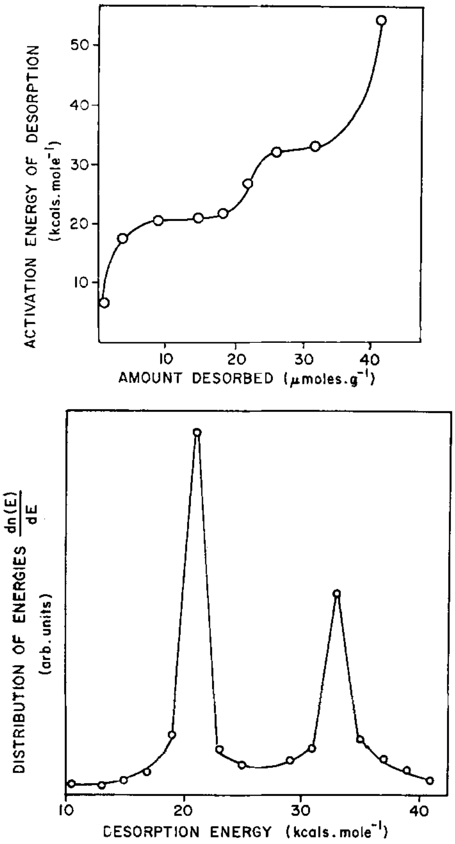

FIG. 9. Variation and distribution of energies observed upon degassing to 550°C.

Tsuchiya, Amenomiya and Cvetanovic (*3*) observed four desorption peaks for the desorption of hydrogen from a platinum surface and interpreted their data in terms of two types of hydrogen atoms adsorbed right on top, and in the interstices between the metal atoms, and two types of molecularly adsorbed hydrogen in the bridged and linear form.

Although the origin of the two types of desorbed hydrogen seems uncertain it is particularly useful to determine the state of the adsorbed hydrogen in relation to its availability, energetically, for participation in catalytic reactions. It is thus apparent that the hydrogen on the cobalt used in this study is in two forms, and will therefore participate in catalytic processes to different extents.

Analysis of the desorption curves corresponding to the transition between the two plateaus and along the 33 kcal/mole plateau of the desorption energy curve showed that the $t_0$ values of the Elovich equation were unusually large (up to 10 min), and are not consistent with the idea of a time delay in the sample reaching the required temperature. At the higher temperatures and energies they again resumed small values found at the lower temperatures.

Further analysis showed that these curves were also capable of giving a linear relationship between the amount desorbed and the square root of time. It is therefore possible that a diffusion mechanism may be controlling the process. Evaluation of the quantities desorbed and the large value of 33 kcal/mole for $E$ suggests that it was not the diffusion out of the pores that is the rate controlling mechanism. A surface migration or diffusion process seems a possible explanation where the hydrogen atom migrates to a site on the surface where it can combine with another atom, and subsequently desorb from it. Another explanation would be the decomposition of a hydride type structure where the hydrogen must diffuse out of the cobalt network before it can desorb.

The temperature range over which this occurs also coincides with a phase change. The transition from hexagonal close-packed $\alpha$-cobalt to face-centered cubic $\beta$-cobalt lies between 340 and 380°C, $\beta$-cobalt being metastable below these temperatures. Cobalt catalysts on reduction have been found to contain the cobalt in the face-centered cubic form (*12*, *13*). Carbiding of the surface and subsequent reduction leaves the cobalt in the $\alpha$-form (*13*). From these observations one may deduce that after the cobalt catalyst used in this study was initially reduced it was in the $\beta$-form. The change in the desorption energetics in Figs. 5–7 may then be associated with the ordering of the cobalt to the $\alpha$-form.

The origin of the hydrogen forming the second plateau (33 kcal/mole) is uncertain. It may have originated from hydrogen bound to the surface or alternatively from the interior of the cobalt crystallites.

Studies conducted with the rutile support, which was treated in the same manner as the catalyst by passing hydrogen over it at 330°C showed negligible quantities of hydrogen desorbed when it was heated between 23 and 550°C. The support did not therefore contribute to the evolution of hydrogen from the catalyst.

## CONCLUSION

The energetics of the surface of cobalt have been shown to change unmistakably during the course of reduction. The existence of two discrete types of sites desorbing hydrogen has been established although their nature is still uncertain. The technique of thermal desorption has been shown to be particularly useful in determining the surface energetics associated with the adsorbed hydrogen, and may prove a useful tool to help establish a relationship between the strength at which the hydrogen is held at the surface, and its participation in catalytic processes.

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